





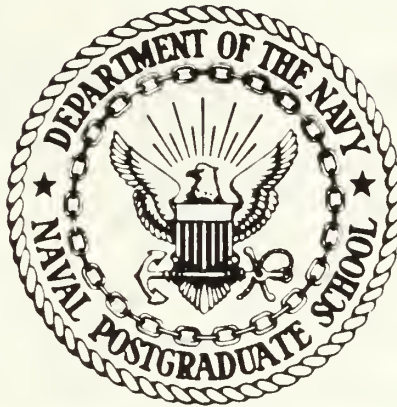
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# NAVAL POSTGRADUATE SCHOOL

## Monterey, California



# THESIS

AN INVESTIGATION OF THE OXIDE ADHESION  
AND GROWTH CHARACTERISTICS ON  
PLATINUM MODIFIED ALUMINIDE COATINGS

by

Margaret Shannon Farrell

September 1986

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T230378



## REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
4 PERFORMING ORGANIZATION REPORT NUMBER(S)			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Naval Postgraduate School		6b OFFICE SYMBOL (If applicable) 69	7a NAME OF MONITORING ORGANIZATION Naval Postgraduate School		
6c ADDRESS (City, State, and ZIP Code) Monterey, California 93943-5000			7b ADDRESS (City, State, and ZIP Code) Monterey, California 93943-5000		
8a NAME OF FUNDING/SPONSORING ORGANIZATION		8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c ADDRESS (City, State, and ZIP Code)			10 SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO	PROJECT NO	TASK NO
			WORK UNIT ACCESSION NO		
11 TITLE (Include Security Classification) AN INVESTIGATION OF THE OXIDE ADHESION AND GROWTH CHARACTERISTICS ON PLATINUM MODIFIED ALUMINIDE COATINGS					
12 PERSONAL AUTHOR(S) Farrell, Margaret Shannon					
13a TYPE OF REPORT Master's Thesis		13b TIME COVERED FROM _____ TO _____		14 DATE OF REPORT (Year, Month, Day) 1986 September	
15 PAGE COUNT 61					
16 SUPPLEMENTARY NOTATION					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Turbine Blade Coatings; Platinum Aluminides; Oxide Adhesion; IN-738; Cyclic Oxidation; Coating Degradation		
19 ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>The operating environment for superalloy blades and vanes in gas turbine engines has necessitated the development of alloy coatings to achieve satisfactory resistance of the metal to oxidation and hot corrosion. Aluminide coatings were initially developed to meet this need. Recently it was shown that platinum additions significantly improve the oxidation resistance of these aluminide coatings. The effects of pre-aluminizing surface smoothness and coating structure for both platinum modified and unmodified aluminide coatings on IN-738 in a cyclic oxidation environment at 1100 C were examined. Weight change measurements were used to determine the coating oxide scale adherence characteristics and to quantify the cyclic oxidation behavior of the various coating structures.</p>					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a NAME OF RESPONSIBLE INDIVIDUAL D.H. Boone			22b TELEPHONE (Include Area Code) 408-646-2551		22c OFFICE SYMBOL 69B1

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An Investigation of the Oxide Adhesion and Growth  
Characteristics on  
Platinum Modified Aluminide Coatings

by

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Submitted in partial fulfillment of the  
requirements for the degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

from the

NAVAL POSTGRADUATE SCHOOL  
September 1986



## ABSTRACT

The operating environment for superalloy blades and vanes in gas turbine engines has necessitated the development of alloy coatings to achieve satisfactory resistance of the metal to oxidation and hot corrosion. Aluminide coatings were initially developed to meet this need. Recently it was shown that platinum additions significantly improve the oxidation resistance of these aluminide coatings. The effects of pre-aluminizing surface smoothness and coating structure for both platinum modified and unmodified aluminide coatings on IN-738 in a cyclic oxidation environment at 1100°C were examined. Weight change measurements were used to determine the coating oxide scale adherence characteristics and to quantify the cyclic oxidation behavior of the various coating structures.

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## I. INTRODUCTION

Gas Turbine engines have become increasingly popular over the last two decades as the main propulsion power plant for United States Naval surface ships. They are also widely used in both civilain and military aircraft as well as in land industrial plants. Gas turbines have numerous advantages as a marine propusion plant but the harsh environment, high temperatures, and low grade fuels have all combined to severely reduce the lifetime of the first and second stage high pressure turbine blades and vanes. The lifetime of these components determines the service and overhaul cycle of the engine which, in turn, dramatically influences the cost of operation.

Coatings were initially proposed to protect the superalloy substrate and enhance its resistance to both high temperature oxidation and hot corrosion. Most of the coatings in use today are nickel aluminide diffusion coatings. These coatings are effective in enhancing the oxidation behavior of the substrate because they provide a source of aluminum which is selectively oxidized to form a layer of  $\text{Al}_2\text{O}_3$ . This is a thermodynamically stable oxide scale which provides a barrier to slow the potentially damaging reaction between the alloy and its environment. This scale is nonminally adherent but it can spall and crack after a relatively short lifetime as a result of thermal cycling or applied stress. This results in an increased oxidation rate and the eventual depletion of the protective elements which react to form the scale. The conventional aluminides have been proven effective in forming this oxide layer but in general they do not possess adequate adhesion characteristics to maintain it over long periods of time in harsh environments.

Platinum plating of the turbine parts prior to aluminizing has been shown to be extremely effective in improving corrosion resistance, even in the harsh marine environment [Refs. 1,2:pp. 192,12]. Originally it was believed that the platinum would provide a diffusion barrier halting the aluminum migration from the surface where it is needed to form the alumina scale. However, it was later shown that the platinum does not form a barrier at all but instead remains concentrated at the surface where it provides a diffusion medium which reacts with the nickel in the substrate to form a nickel aluminide subsurface structure [Ref. 2:p. 8]. Although the platinum addition did not cause the formation of a diffusion barrier it nevertheless enhanced the oxidation

resistance of the coating by promoting the slow growth of an extremely adherent stable oxide. Significant improvement in lifetimes of platinum plated aluminized gas turbine components exposed to severe thermal and mechanical stresses have been recorded and confirm the effectiveness of the platinum modified coatings for high temperature corrosion protection [Refs. 3,4:pp. 25,5].

The purpose of this thesis was to examine the oxide adherence characteristics of the platinum modified aluminum diffusion coatings on the superalloy IN-738. Specifically, the effects of pre-aluminizing surface roughness and coating structure were studied in a cyclic oxidation environment to determine the influence of these factors on oxide scale growth and adherence.

## II. BACKGROUND

### A. HIGH TEMPERATURE CORROSION

#### 1. Hot Corrosion

Hot Corrosion is defined as the combined attack of high temperature combustion exhaust gases and condensed phases on the surface of a component [Ref. 3:p. 17]. Marine gas turbines are particularly sensitive to this form of accelerated substrate attack as a result of their high operating temperatures and the presence of contaminants such as sulfur, sulfates, and chlorides from ingested fuel and air. It is the major cause of failure of the high pressure turbine blades and vanes in these engines and as a result is the object of extensive research. There are several forms of hot corrosion attack which contribute to the airfoil deterioration. The most detrimental of these are high temperature hot corrosion, low temperature hot corrosion and high temperature oxidation.

It was originally thought that for hot corrosion to occur the temperature of the environment must be at or near the melting point of  $\text{Na}_2\text{SO}_4$  so that the molten salt could condense on the blade surface [Ref. 5:p. 476]. However, operating experience with marine gas turbine engines showed that very high levels of corrosion were experienced by vessels operating at relatively low power, in the temperature range of approximately 600-800°C [Ref. 6]. It is this corrosion attack that has been defined as Low Temperature or Type II hot corrosion (LTHC). It is generally recognized by its pitting mode of attack. Type I or High Temperature Hot Corrosion (HTHC) refers to the corrosion attack observed on components operating in the 800-1000°C range. The mechanisms for corrosion in each of these two cases are different and have been the subject of research over the years in order to develop coatings that are effective in preventing both.

Hot corrosion can be categorized as basically a two stage process. During the initiation stage the elements in the coating are oxidized, forming an initially protective scale which remains intact until the element being selectively oxidized is depleted. The rate of surface degradation during this stage is relatively slow and depends on the operating environment, temperature and alloy composition. This phase of hot corrosion is the same for both HTHC and LTHC.



The second stage of hot corrosion attack proceeds much faster than the first and involves reactions with deposited materials on the component surface. It is during this stage of hot corrosion attack that differences can be observed between the degradation due to LTHC and that due to HTHC. Sodium salts, present in the engine intake air, react with sulfur in the fuel to form sodium sulfate. Vanadium, found in many of the low grade fuels used in marine gas turbines, forms a molten slag layer which fluxes the protective oxide resulting in direct oxidation of the metal. The salt fluxing reactions can be either basic or acidic. Basic fluxing occurs when there is a reaction between the oxide ions in the deposit and the protective oxide scale, whereas acidic fluxing involves the donation of oxide ions by the oxide scale to the deposit. In either case, the oxide scale is rendered nonprotective. The acidic fluxing reaction can be further subdivided as either gas phase or alloy induced, depending on the source of the acidic component. The hot corrosion degradation observed on a component may result from any of the degradation mechanisms presented but they are generally only significant at high temperatures. [Ref. 7:pp. 609-611]

The mechanism for low temperature hot corrosion is not as well understood but it has been established that it is primarily related to the presence of sulphur trioxide which, at these lower temperatures, suppresses the melting point of sodium sulfate and results in accelerated sulfur transfer through the melt. A gas phase induced acidic fluxing reaction takes place and accounts for the difference in corrosion behavior observed in the two temperature regimes. [Refs. 8,9:pp. 15,8]

## **2. High Temperature Oxidation**

High temperature oxidation of the superalloy materials used in gas turbine engines is a very important form of high temperature corrosion which severely affects the material's lifetime and performance. An alloy exposed to high temperatures in an oxygen environment will form oxides of all the elements in the alloy providing the oxygen pressure in the gas is greater than the metal-metal equilibrium pressure for each of the alloying elements. The result of this reaction will be the rapid formation of various oxides on the surface of the component but the limited supply of oxygen in the oxidizing atmosphere will cause competition between these oxides until those that are the most stable dominate. This will cause an oxide scale formation usually composed of numerous oxides but with the most stable adhering directly to the substrate or coating surface. This formation process continues until the point where it becomes more favorable for the oxide to grow laterally, eventually forming a continuous layer

over the entire surface of the alloy. This stage of the oxidation process has been termed transient oxidation and varies in the length of time it takes to complete. Depending on the temperature, the alloy and its environment it could take anywhere from several seconds to several days. [Ref. 7:pp. 603-605]

After the transient growth stage is complete the oxidation resistant alloy enters a steady state period of oxide growth. It is the duration of this stage that determines the ability of a material to withstand damage from the severely oxidizing environment over an extended period of time. During this stage the protective oxide grows in accordance with the parabolic rate law and remains intact on the component surface. The oxide then provides a barrier between the substrate and its environment which enables the component to withstand potentially damaging conditions.

The continuous oxide scale that grows on the component surface during the steady state phase of oxidation will eventually become damaged in service, usually the result of thermally or mechanically induced stresses. This damage is primarily seen as spalling and cracking of the scale. When the alloy is later exposed to the oxidizing environment it must once again go through the transient oxidation stage and reform the most thermodynamically stable oxide where it had spalled. This accelerated growth in localized areas, in addition to the steady state growth, causes the depletion of the elements that are being selectively oxidized to form the protective scale. With each repetition of this process the transient period becomes longer and eventually the alloy will no longer be able to selectively oxidize the same element as a continuous layer over the entire component surface. Less stable oxides form at this point and no longer provide the protection afforded by the adherent, slowly growing oxides which first formed on the surface. At this point the breakaway region of oxide growth is entered and the oxidation rate increases dramatically. The result of this process is severe degradation of both the coating and the substrate. [Ref. 7:pp. 605-607]

## **B. COATINGS FOR CORROSION PROTECTION**

The high temperature corrosion environment in which gas turbine blades and vanes generally operate has necessitated the development of protective coatings to prolong the life of these superalloy components. These superalloys, generally of nickel and cobalt based compositions, were developed to optimize the mechanical and physical properties to match the mechanical and thermal loading requirements of the particular application. As a result of these design requirements, the oxidation and hot

corrosion resistance of the alloys themselves is insufficient to protect the alloy from accelerated service degradation. The most common forms of commercially available coatings today are the overlay, the thermal barrier and the diffusion type. Regardless of the type of coating used, the purpose is the same: to restore and/or enhance the oxidation and hot corrosion resistance of the superalloy. This is accomplished by the formation of stable oxide scales which provide a reaction barrier with the environment and maintain that barrier during operation in potentially damaging environments.

## C. COATING TECHNOLOGY

### 1. Aluminum Diffusion Coatings

Aluminum diffusion coatings are widely used in marine and aircraft gas turbine engines and they have been proven effective in retarding high temperature corrosion damage. The principal function of these coatings on superalloys is to provide the source of aluminum for the formation of  $\text{Al}_2\text{O}_3$  and other protective oxides while not detrimentally affecting the substrate's mechanical properties [Ref. 10:p. 546]. These coatings have typically been divided into two categories: Low Temperature High Activity (LTHA), and High Temperature Low Activity (HTLA).

#### *a. Low Temperature High Activity Aluminum Diffusion Coatings*

The basic distinguishing characteristic of the coating is that it involves the inward diffusion of aluminum into the alloy to form the protective layer. It is usually produced using a high activity source of aluminum which initiates a competitive growth process involving the  $\epsilon(\text{NiAl}_3)$  and  $\delta(\text{Ni}_2\text{Al}_3)$  phases. This diffusion reaction results in the rapid formation of a coating zone composed primarily of the  $\delta$  phase [Ref. 10:p. 548]. The initial surface of the substrate corresponds to the surface of the aluminum rich coating and therefore, stable particles adhering to the specimen surface before the aluminizing treatment will remain there. These particles act as markers and enable the confirmation of the inward mode of formation of this particular coating. In addition, the elements of the substrate that are not soluble in the  $\delta$  phase will form precipitates. These precipitates, along with other stable particles, such as carbides present prior to the aluminizing process, will remain embedded in the  $\text{Ni}_2\text{Al}_3$  layer. The presence of these particles also serves distinguish this type of coating. [Ref. 11:p. 279]

Although a coating formed by this process has the aluminum source at the surface to enhance the formation of the alumina scale, it is of no practical use in the as-formed state because it has a very low melting point and is relatively brittle.



Further heat treatment of the coating is therefore carried out without the presence of an external aluminum source so that the as formed coating reacts with the substrate to effect the growth of the  $\beta(\text{NiAl})$  phase. The NiAl coating formed by this process can easily be identified by the three layer coating structure. The first layer is an external zone which is almost as thick as the initial  $\text{Ni}_2\text{Al}_3$  layer and which has precipitates distributed throughout. The central section is devoid of precipitates and is often called the "denuded" region. The internal zone consists primarily of precipitates and carbides distributed in an NiAl matrix. [Refs. 10,11:pp. 551,280]

#### ***b. High Temperature Low Activity Aluminum Diffusion Coatings***

The High Temperature Low Activity process of aluminizing superalloys is also widely used as a commercial coating procedure. It is characterized by the outward diffusion of nickel from the substrate into the aluminized layer. This is generally accomplished in a pack cementation process, as with the LTHA process, but in this case a "low activity medium" is employed. This is accomplished by using low aluminum contents in the pack at a high temperature and/or by using aluminum alloys in the pack instead of pure aluminum [Ref. 10:p. 553]. This reaction causes the direct formation of the  $\beta$  phase with no additional heat treatment required. Unlike the case of the LTHA coating, the initial surface of the specimen is located within the coating after the aluminizing process. This coating can be described as having two zones, one on either side of the initial surface. The external zone is formed primarily by the outward diffusion of nickel in the NiAl layer while the internal zone is formed through denudation of nickel from the substrate, resulting in a region rich in the elements of the substrate with the exception of nickel [Ref. 11:p. 275]. Although this process caused the direct formation of the  $\beta$  protective phase it takes significantly longer to form than does the inward type because the nickel diffusion in NiAl is relatively slow. This requires that higher temperatures and longer diffusion times be used to effectively form the protective coating layer [Ref. 10:p. 553].

#### **2. Platinum Modified Aluminide Diffusion Coatings**

Platinum modified aluminum diffusion coatings were initially developed to enhance the oxidation and hot corrosion resistance of superalloy components by providing a diffusion barrier to prevent the migration of the aluminum on the surface into the substrate. Platinum was selected as an effective diffusion barrier because it is soluble in most nickel based superalloys, its atomic radius is sufficiently different from that of aluminum, it has a high melting point, it has good high temperature oxidation



resistance and it can be deposited on a component using relatively easy methods [Ref. 1:p. 191]. Later it was found that the platinum does not form a diffusion barrier to the aluminum inward migration but instead remains concentrated in the outer part of the coating [Ref. 12:p. 6]. Nevertheless, the benefits of platinum modified aluminum coatings are well documented and their effectiveness in enhancing the alumina oxide scale adherence is significant. It has been postulated that since platinum and aluminum have such great affinity for each other, the platinum might be so effective because it inhibits the aluminum migration by causing the driving force for interdiffusion to be decreased [Ref. 13:p. 168]. It has also been proposed that the enhanced oxidation behavior of the platinum aluminides might be due to the irregular oxide substrate interface resulting from the development of protrusions during the pre-aluminizing diffusion which extend into the oxide scales [Ref. 14:p. 518].

Platinum modified aluminum coatings are formed by first applying a thin layer of platinum directly on the substrate surface. Various methods are available for accomplishing this [Ref. 15:p. 223], but electrodeposition is the most common commercially used technique. The method of platinum application significantly affects the structure of the platinum plated surface. Generally, however, regardless of processing technique, the surface is very rough, exhibiting almost a "cauliflower" type structure [Ref. 16:p. 2558]. Figure B.1a shows an example of a commercially obtained platinum plated surface on a nickel based superalloy.

After the initial platinum plate is applied, a diffusion process is normally conducted prior to the aluminizing. This heat treatment facilitates the platinum bonding and diffusion into the substrate and changes the surface platinum content. The duration of this heat treatment and the temperature at which it is conducted have a significant impact on the eventual structure of the coating formed in the aluminizing process [Refs. 17,18:pp. 6-11,5]. The heat treatment has also been shown to have an effect on the surface structure of the platinum plate. Boone et al. have shown that the surface becomes even rougher than the original cauliflower type structure with increasing time and temperature of diffusion heat treatment [Ref. 16:p. 2558]. Figure B.1b shows a platinum plated surface on a nickel based superalloy obtained from a commercial manufacturer that has been heat treated for two hours at 980°C.

As with the conventional aluminide coatings, the platinum modified coatings can generally be categorized according to structure as inward, formed by the LTHA process, and outward, formed by the HTLA process. The method of application of the

aluminum coatings is the same as described for the simple aluminides. Also, as before, those components which received the LTHA aluminizing process must undergo the additional heat treatment to improve the coating properties.

The structures of the coatings produced now depend not only on the aluminizing process but also on the amount of platinum deposited and the pre-aluminizing diffusion process. Streiff et al. have shown that the structure for the platinum modified aluminides with the HTLA aluminizing process ranges from a single phase  $\text{PtAl}_2$  for a specimen subject to the minimum platinum diffusion (1/2 hour at  $870^\circ\text{C}$ ) to a two phase,  $\text{NiAl}$  plus  $\text{PtAl}_2$  for those subject to longer diffusion times at higher temperatures. In all of these low activity coatings, grit particles (when present) are found throughout the inner coating zone. As with the unmodified aluminides, these particles serve as inert markers that show that growth is predominantly by the outward diffusion of nickel. [Ref. 17:p. 6]

In the high activity coatings, the structure ranges from an outer layer with high platinum content consisting primarily of  $\text{PtAl}_2$  for the shortest platinum diffusion times to a lower platinum content layer with a two phase structure for those experiencing longer diffusion at higher temperatures. The grit particles resulting from the initial surface in this case remain localized in a shallow zone underneath the surface indicating that the coating grows primarily by the inward diffusion of aluminum, as would be expected for a high activity coating. [Ref. 17:p. 9]

The mechanisms for formation of any of these coating structures is extremely complex but significant research has been undertaken recently to relate the coating structure variable with performance in hot corrosion and oxidation tests. Deb et al. have described the coating formation process in detail and they outlined the resulting range of coating structures [Ref. 18:p. 5-7]. These processing differences have been shown to affect not only the structure but also the surface roughness. It is this surface roughness effect that has received significant attention in possibly explaining the very adhesive  $\text{Al}_2\text{O}_3$  formed on the platinum aluminide coatings.

#### **D. PROTECTIVE OXIDE GROWTH AND ADHESION**

It has been established that the benefit derived from the platinum addition to aluminide coatings is related, at least in part, to the increased adherence of the protective alumina scale. The mechanisms of formation and growth, and their influence on increased adherence, however, are not yet fully understood and have been

the object of extensive research. The relationship between scale growth, microstructure, and the oxide-substrate interface characteristics must be considered to understand the reaction that leads to the development of an adherent protective oxide scale.

Felten and Pettit have examined the development and growth of  $\text{Al}_2\text{O}_3$  on several platinum aluminum alloys and found that both the growth rate of the scale and the oxidation rate of the alloy depend on the microstructure of the scale. However, the microstructure of the scale is closely related to the mechanism of scale growth and dependent on the phase of the alloy being oxidized. On the Pt-6Al alloy, which is composed of two phases, it was observed that the oxide over the  $\text{Pt}_5\text{Al}_3$  phase formed by outward growth and on the  $\text{Pt}_2\text{Al}$  phase by inward growth. The initial oxide formed over the surface showed numerous coarse platinum nodules and finer oxide nodules which were eventually incorporated into the oxide scale with time at temperature. They also noted that there was a difference in the type of oxide protrusions present, the resulting grain structure, and the oxide scale thickness for each of the two phases being oxidized. The temperature of the oxidizing environment was found to affect the oxide morphology, with the oxide surface becoming rougher and smaller grained with decreasing temperature. [Ref. 19:pp. 195-207]

On the Pt-2Al alloy, which is also composed of two phases, the structures of the oxide formed did not appear to be a function of the phase being oxidized. In the transient oxidation regime in air this alloy formed particulate  $\text{Al}_2\text{O}_3$  in a platinum matrix. With increasing time at temperature, a smooth continuous layer of  $\text{Al}_2\text{O}_3$  was developed but still contained mounds of platinum and particulate  $\text{Al}_2\text{O}_3$ . The grain size was determined to be fairly uniform throughout and similar in size and structure to that formed over the  $\text{Pt}_2\text{Al}$  phase on the Pt-6Al alloy. The effect of aluminum concentration, though not significant in the Pt-2Al alloy, was found in examination of the oxidation behavior of the Pt-.5Al alloy, where the  $\text{Al}_2\text{O}_3$  which developed on the alloy surface was only semicontinuous. [Ref. 19:pp. 192,210]

The growth of the  $\text{Al}_2\text{O}_3$  scales on each of the alloys examined confirmed that oxide growth is a grain boundary controlled transport process during which the oxygen diffuses inward along grain boundaries [Ref. 19:p. 221]. This conclusion is also supported by the work of Allam et al. who observed that there was considerable variation in grain size through the scale thickness with fine grains in the outermost part and relatively large, columnar grains in contact with the alloy. They proposed that the



fine grains result from initially nucleated oxide while the inner, columnar grains, are formed later when the overall thickening rate of the oxide scale is low. [Ref. 20]

On the mechanisms of oxide scale adherence, Fountain et al. have found that a platinum stabilized adherent scale formed on the surface of a nickel based alloy which was oxidized alongside a piece of platinum at high temperature. This scale was seen to be highly convoluted, with whisker-like protrusions from the surface of the oxide. They concluded that the platinum does influence the growth mechanism and substructure to an extent, but they do not attribute the stability of the formed  $\text{Al}_2\text{O}_3$  to increased adherence between the alloy and the substrate. Instead, they suggest that the beneficial effects of the platinum addition might be due to the platinum influence on the stress relief mechanism at temperature by enhancing either the diffusion creep process or grain boundary sliding, or possibly that it reduces oxidation growth stress generation. [Ref. 21:pp. 342-345]

The development of inwardly growing  $\text{Al}_2\text{O}_3$  pegs which act to anchor the scale to the substrate at the oxide-substrate interface has been proposed as a significant factor accounting for the "rare earth effect" of promoting oxide adhesion. In a recent study [Ref. 14:p. 527], Allam et al. found that oxide pegs did not develop in alloys containing small platinum additions but did in an alloy with both platinum and hafnium. On exposure to an oxidizing environment, the alloy with both platinum and hafnium additions showed a significant improvement in both isothermal and cyclic high temperature oxidation tests. This is attributed to the regular distribution of oxide pegs at the oxide substrate interface. It has been shown [Ref. 22], that the distribution of the oxide pegs is a function of the distribution of the active element in the substrate, with hafnium addition able to produce a more regular distribution than yttrium additions.

In an investigation of the effects of platinum on a nickel based superalloy, Felten found that small platinum additions were effective in promoting oxide scale adherence in a cyclic oxidation environment and that the improvement was directly related to the amount of platinum in the alloy. It was also noted that the presence of platinum positively influenced the reformation of  $\text{Al}_2\text{O}_3$  scale after spalling had occurred. [Ref. 23]

The exact reasons for the increased oxide adhesion characteristics of alloys containing platinum, or similarly, platinum modified aluminide diffusion coatings, have yet to be definitively determined. However, the existence of a convoluted



oxide-substrate interface and the ability of the platinum influenced oxide to grow laterally over it, has been well established and sets the platinum effect apart from that of the rare earth additions. This investigation will examine how the roughness of the substrate surface affects the eventual growth and adhesion of the  $\text{Al}_2\text{O}_3$  scale in the cyclic oxidation environment.

### III. EXPERIMENTAL PROCEDURE

#### A. SPECIMEN PREPARATION

All specimens used in this experiment were prepared from commercially obtained 0.7 cm diameter pins of the nickel based superalloy IN-738. The nominal composition of this superalloy by weight percent is presented in Table I. These pins were cut to approximately 0.3 cm lengths and then tumbled in a mixture of water and ceramic beads to eliminate the sharp edges, thereby providing an initially smooth surface for coating. A hole of approximately 0.9 mm diameter was spark machined through each specimen so that it could be hung during the platinum plating process. This was done to ensure that each specimen was evenly coated with platinum over the entire surface.

The pins were electroplated with platinum to a thickness of 7.0-8.0  $\mu\text{m}$ . Each pin was then encapsulated in quartz tubing, vacuum sealed and subjected to one of the heat treatments outlined in Table II. The specimens were then designated as either "smooth" or "rough". Those specimens designated as "smooth" were polished using a hand polishing tool with assorted felt buffing tips and diamond paste abrasive compounds. Scanning electron photomicrographs were taken during this stage of processing in order to document the degree of smoothness being achieved. Figure B.2 shows the "smoothed" surface of one of the platinum plated specimens.

The samples were then aluminized; both high temperature low activity and low temperature high activity processes were used. Two additional specimens were added to this group to provide a basis for comparison. These specimens were IN-738 pins with no platinum plating; each one received a different aluminizing treatment. Specimens were then numbered using the code outlined in Table III; they were subsequently weighed, measured, and photomicrographed. Only ten of the available sixteen specimens were selected for testing. The specimens that had received the minimum platinum diffusion and the inward coating spalled excessively and were unfit for gravimetric studies. Also, several of the two phase structures were not examined because it was felt the sufficient data could be obtained from the ones selected since the coating--surface morphology was not significantly different. The list of specimens examined is presented in Table IV. Specimens were then weighed and measured with this data serving as the original on which all gravimetric calculations were based.

## **B. EXPERIMENTAL TESTING**

Cyclic oxidation testing was conducted in a vertical furnace rig as shown in Figure B.3. Specimens were placed in ceramic specimen holders and cycled under atmospheric conditions for cycles consisting of 60 minutes in the hot zone at 1100°C and 10 minutes out of the furnace. The heating and cooling cycle is also shown in Figure B.3. The specimens were removed for weight gain measurement and visual examination at appropriate time intervals throughout the testing. Each of the specimens received a total of 275 cycles at temperature.

At the completion of the cyclic testing the specimens were cut and prepared for examination under the scanning electron microscope. Both cross sectional and surface photomicrographs were taken of each specimen.

## **C. DATA ANALYSIS**

The weight change data recorded at the various intervals were plotted versus time with the data being fit to a smooth curve using a least squares polynomial curve fit procedure. To confirm the parabolic nature of the oxide growth, the square of the weight change was plotted versus time and a straight line was fit to these points, again using a least squares curve fit. From this curve, the value of the parabolic oxidation rate constant,  $K_p$ , was determined. Scanning electron photomicrographs were taken of the cycled specimens to analyse the surface changes and the coating structure after degradation.

## IV. RESULTS AND DISCUSSION

### A. WEIGHT CHANGE ANALYSIS

The weight change data obtained in the cyclic oxidation experiments is presented in Figures B.4 through B.15 for both the platinum modified and the conventional aluminide coatings. Upon initial examination, it is apparent that the platinum aluminide coatings demonstrated significantly improved oxidation resistance and in general, remained protective throughout the oxidation period.

The coatings on specimens R1IIB and S1IIB were initially formed with minimum pre-aluminizing platinum diffusion and the outward type aluminizing process producing a thin, continuous layer believed to be  $\text{PtAl}_2$ . The oxidation behavior shown through weight change measurements, Figures B.4 and B.5, appears to be essentially parabolic through the steady state region. The rough specimen, R1IIB, exhibited a lower growth rate over the 275 hours and a maximum weight change of only  $0.73 \text{ mg/cm}^2$ . The smooth specimen, on the other hand, had a higher oxide growth rate which increased significantly after only 175 hours of cyclic exposure. This increase is believed to be caused by the oxide reformation in areas that had spalled. The accelerated growth necessary to reform the protective layer appears to have progressed to the point where the aluminum was sufficiently depleted from the coating and after only 225 cycles it failed, exhibiting a significant amount of weight loss in subsequent cycles. It would appear that the mechanical smoothing process adversely affected the oxidation growth and adherence of the protective oxide on this particular coating. This observation was verified subsequently in metallographic examination. The inability to quantify the amount of smoothing achieved on the samples appears to be a factor here because in the polishing process some of the platinum rich surface layer might have been polished off. This could have resulted in eliminating the benefits derived from the platinum addition, causing the coating to oxidize in a manner more characteristic of the conventional aluminides after an extended period of time at high temperature.

Specimens consisting of the single phase structure but subject to the inward aluminizing process were also prepared for examination in this experiment. At room temperature, before any cyclic oxidation exposure, spontaneous delamination of the platinum plating was observed. Manley [Ref. 24:pp. 35-36], noted the same behavior in



specimens subjected to the minimum diffusion time and temperature. He postulated that the delamination was the result of thermal gradient strains enhanced by the brittleness and coefficient of thermal expansion mismatch between the electrodeposited layer and the specimen substrate and the resulting stresses built up during cooling from the processing temperature. Because specimens of sufficient quality for gravimetric study could not be obtained, they were not examined in this experiment.

Specimens R2IIB and S2IIB were subject to a mid-range platinum diffusion heat treatment as shown in Table II and then aluminized using the HTLA process. As observed in the first set of specimens, the rough specimen exhibited an initial period of rapid growth during the first hour and then demonstrated parabolic growth kinetics over the subsequent cycles. The smooth specimen had a higher rate of weight change over the duration of the test and again showed significant weight loss after only 225 hours of testing. The loss of platinum on the surface during the polishing process, as explained previously, seems to account for the coating degradation observed.

The inward coating formed on specimens R1IIA and S1IIA showed almost no difference in cyclic oxidation behavior over the entire testing period. The amount of rapid growth observed during the first few hours was slightly larger for the rough specimen and then the oxide grew on both in similar proportions for the 275 cycles. The curves do not indicate spalling behavior for either of the specimens but they do show that there was a higher overall weight gain (almost  $1.0 \text{ mg/cm}^2$ ) which occurred at a faster rate in this case than that observed for the outward type coatings previously described. This could be due to the fact that there is a lower platinum level in this coating than in those formed by the outward aluminizing process.

Specimens R3IIB and S3IIB were subject to the same platinum diffusion heat treatment as those just described but they received the outward aluminizing procedure. A substantial difference can be seen in the weight change behavior of these specimens but again, it is the rough specimen that exhibits the distinctly parabolic growth indicative of protective oxide scale development. The smooth sample had a significantly higher weight change in the first hour and then continued to grow at a much faster rate over the duration of the experiment. In both cases, however, the oxide developed appears to be highly adherent with no spalling behavior observable through the weight change measurements. It would be expected however, that the rapid growth exhibited by the smooth specimen could only be sustained for a short period due to the limited source of aluminum in the coating. The failure of this

coating would be expected before the failure of the coating with the similar structure but the rough platinum surface.

Specimens R4IIB and S4IIB received the maximum pre-aluminizing platinum diffusion and the outward aluminizing process. The weight change behavior in this case was extremely different from that observed for the other platinum modified coatings examined. The oxide scale developed on the rough specimen grew very quickly during the first hours of oxidation exposure and then continued to grow in a linear fashion over the duration of the test. This could be the result of excessive scale cracking and spallation requiring the continual redevelopment of an oxide layer at the surface. The reason for the difference observed in this case cannot be explained by the weight change data and it is possible that this coating had received some sort of damage prior to thermal cycling which caused the abnormal and unexpected behavior. In contrast to the oxide development observed on the rough specimen, the smoother sample showed a very slow rate of oxide growth throughout the duration of the test and appeared to develop a highly adherent protective scale.

The conventional aluminides demonstrated a significantly different weight change behavior than the platinum modified coatings. For both the inward and outward coatings, the initial growth in the first hours was very small and the total weight gain observed on either specimen only ranged up to about  $0.4 \text{ mg/cm}^2$ . This was much smaller than that observed on the coatings containing platinum. The inward coating began to lose weight after only 35 hours of testing and that trend continued throughout subsequent cycling. The outward coating lasted somewhat longer, not demonstrating severe degradation until about 150 hours of exposure.

Analysis of the weight change data supports the conclusion that the addition of platinum to diffusion aluminide coatings enhances the high temperature oxidation behavior by promoting the slow growth of a highly adherent oxide on the surface of the component. The roughness of the platinum surface appears to affect the growth kinetics of the scale so that a more adherent, slower growing oxide layer is formed. This is the desired growth kinetic because for a slowly growing scale, the Al depletion will be slight, enabling the reformation of protective oxides should the first layer become damaged in service. Although the weight change data involved the surface area calculation so that comparisons could be made, it does not account for the fact that the surface area of the rough specimens is larger than that of the smooth specimens due to the microscopic roughness not able to be quantitized. If this effect is

taken into consideration, it would appear that the rough specimens are even more effective in promoting slow oxide growth.

The parabolic oxidation rate for each of the platinum modified coatings was calculated by plotting the square of the weight change versus time and fitting the data to a linear curve. The values obtained for  $K_p$  are presented in Table V. As was noted previously, in all but one case, the growth rate for the rough specimens with the outward type coating was significantly smaller than that for the smoother specimen of the same structure. For the inward coating, there was little difference between the values obtained for the smooth and rough specimens. Whittle and Hindam summarized the available  $K_p$  data for various alumina formers [Ref. 25:p. 89], and the data obtained in this study falls within their scatter band at 1100°C with only one exception, specimen R4IIB which was a questionable sample. This confirms that the oxidation behavior observed is typical of  $Al_2O_3$  growth at high temperatures.

## B. SURFACE ANALYSIS

The specimens were examined at various times during the cyclic testing for macroscopic changes at the surface. During the early stages of high temperature exposure, all specimens demonstrated effects from segregation in the alloy. These effects were manifested as white "spots" over the surface of the cast sample. The baseline structures developed these spots within the first five hours and they were incorporated into the continuous oxide scale by the twenty fifth hour of oxidation. The platinum modified structures showed significant differences in the formation of the spots. On the coatings subjected to the minimum platinum diffusion heat treatment they were large and persisted for about 125 hours of testing. Figure B.16a shows the segregation effects on specimen S1IIB after 50 hours of exposure. For the two phase structures, formed through increased platinum diffusion, the segregation effects were seen as many small spots distributed over the entire surface of the specimen. This effect can be seen in Figure B.16b. It was also noted that the effect persisted over about 150 cycles. No difference in the substrate segregation effects was noted for the smooth versus rough specimens. It would appear that the platinum acts to block the selective diffusion of certain elements in the substrate.

The surface morphology observed on the specimens varied widely after 275 hours of cyclic oxidation testing. Some spalling was observed on all specimens, except S2IIB, BLA and BLB which were seen to spall excessively. Figures B.17 and B.18 show this



spalling behavior. It should be noted that the spalling on specimen S2IIB was localized, confined to a fairly small area on one side of the specimen. This is probably the result of excessive polishing which depleted the surface of the protective platinum plate. This observation is supported by the weight change data, as is the spalling behavior of the baseline structures.

Surface deformation, described as rumpling by Manley [Ref. 24:p. 38], was observed and can be seen in Figures B.17 through B.19. Examination of the surface photomicrographs for all of the specimens reveals that the surface deformation after 275 cycles was not affected by the pre-aluminizing surface roughness. Figure B.19 shows the range of surface structures obtained for the platinum modified coatings after testing. Specimen S2IIB exhibited a fairly smooth surface morphology and the opposite, a very rough surface, is observed for specimen R3IIA. It is important to note, however that generalizations about smoothness and roughness of the cycled specimens cannot be made from these photomicrographs alone; a full range of structures, of which these represent the extremes, was observed for both sets of specimens regardless of the pre-aluminizing surface treatment. It is also interesting to note that a significant amount of surface deformation was observed on the baseline structures. This can be seen in Figure B.18.

### C. COATING STRUCTURE DEGRADATION

Weight change measurements alone are not a reliable criterion upon which to evaluate the effectiveness of a coating's behavior in oxidation testing. Therefore, metallographic examination of each of the specimens was conducted to observe the changes and degradation after 275 hours of cyclic exposure in a high temperature oxidizing environment.

Cross section Scanning Electron Microscope (SEM) photomicrographs of specimens R1IIB and S1IIB are presented in Figure B.20. These show very little difference between the smooth and rough samples, both in coating structure and surface deformation. There is, however, a small difference observed in the thickness of the aluminum depleted phase present at the surface of the coating. This difference may be the result of the coating degradation of the smooth specimen revealed in the weight change data. Also, in this and all other platinum containing coatings there appears to be no loss of the protective "reservoir" phase, platinum rich NiAl, in the inner zone of the coating. Ternary phase stability of the NiAl phase as affected by the platinum additions may explain this observation in the platinum modified coatings.



The SEM photomicrographs for specimens R2IIB and S2IIB, presented in Figure B.21, show a significant difference in coating degradation after cyclic oxidation exposure. In the coating on the smooth specimen, the  $\gamma'$ ,  $\gamma$  and  $\beta$  phases are distinctly obvious. The presence of the  $\gamma'$  phase in the coating is significant because it indicates a reduction in the aluminum level within the coating and therefore, restricts the ability of the coating to reform  $\text{Al}_2\text{O}_3$  after spalling or cracking. The presence of the platinum in the coating is generally believed to affect the aluminum reduction mechanism, whether it be by interdiffusion or by spalling, and therefore, limit the amount of  $\gamma'$  formation. This, obviously, did not happen in the case of specimen S2IIB. It was previously proposed, during the analysis of the weight change measurement for this specimen, that excessive polishing might have damaged or even removed the platinum layer at the surface. This argument is supported by examination of the coating structure photomicrograph which shows that this particular coating degraded in a manner very similar to that observed for the unmodified aluminide coatings.

SEM photomicrographs of specimens R3IIA, S3IIA, R3IIB and S3IIB are presented in Figures B.22 and B.23. Very little difference can be seen in any of these structures. There is no  $\gamma'$  formation which would indicate accelerated degradation and the protective reservoir phase appears to have remained intact throughout the test. Surface deformation is not very different here between the rough and smooth specimens but it does appear to be slightly greater for the inward type coating. A significant amount of coating porosity can be seen in these structures and it is believed to result from the pre-aluminizing platinum diffusion heat treatment. In comparison with the other structures, it appears that the amount of porosity increases with increasing platinum diffusion into the substrate as would be expected from Kirkendall porosity found during pre-aluminizing diffusion.

Analysis of the cross section photomicrographs of specimens R4IIB and S4IIB which are presented in Figure B.24, reveals some features which may account for the differences observed in the weight change behavior of those specimens. For the rough sample, it appears that there is some  $\gamma'$  precipitation within the protective  $\beta$  phase. The weight change data indicated linear growth characteristics throughout the testing period. It is therefore reasonable to assume that a significant amount of  $\text{Al}_2\text{O}_3$  reformation occurred as a result of some form of oxide degradation. The aluminum present in the coating can only be expected to sustain rapid growth over a limited

period of time before it becomes sufficiently depleted and no longer provides protectivity. The  $\gamma'$  formation has not progressed to the point observed in specimen S2IIB where a continuous layer of  $\gamma'$  was present, but it does appear that the initial stages of that same type of degradation mechanism are in effect with this specimen. Specimen S4IIB shows no degradation; this is in agreement with the weight change data.

As expected, the coating structures of the conventional aluminides were very different from those observed in the platinum modified coatings. For both the inward and outward baseline structures, shown in Figure B.25, the  $\gamma$ ,  $\gamma'$ , and  $\beta$  phases are distinctly obvious and the protective "reservoir" phase observed in the platinum modified structures is not evident. "Spikes" of  $\gamma'$  can be seen extending from the surface of the coating down into the substrate itself. As described earlier, this precipitation of  $\gamma'$  indicates a decrease in the aluminum level in the coating and inhibits the repeated formation of  $\text{Al}_2\text{O}_3$  at the surface of the coating. It also can act as a "pipeline" for detrimental substrate elements to rapidly move to the surface and promote  $\text{Al}_2\text{O}_3$  breakdown. Both the microscopically observed excessive spalling, Figure B.18, and the weight change data support the relationship between coating degradation and  $\gamma'$  formation. It has yet to be determined however, whether the precipitation of  $\gamma'$  in the coating leads to the destruction of the protective oxide and subsequent accelerated substrate attack or whether the loss of protective oxide causes the  $\gamma'$  precipitation.

## V. CONCLUSIONS AND RECOMMENDATIONS

The results of these experiments and the subsequent discussion support the following conclusions:

- 1 Platinum modified aluminide coatings showed significant improvement in oxide adherence over the conventional aluminides for both the inward and outward aluminizing processes tested in a cyclic oxidation environment at 1100°C.
- 2 Coating structural degradation was significantly different for the platinum modified aluminide coatings. Improved oxide adherence may account for the fact that there was minimal  $\gamma'$  phase observed, but that has not been proven; only the existence of a  $\gamma'$  phase can be linked to coating failure.
- 3 Coating porosity, which was possibly the effect of initial porosity formed during the platinum-substrate interdiffusion, was observed and found to vary directly with the amount of platinum diffusion.
- 4 Substrate segregation effects on oxide composition and performance were markedly affected by the presence of platinum and found to vary directly with the amount of pre-aluminizing platinum diffusion.
- 5 The pre-aluminizing surface smoothness had only a limited effect on the total weight change experienced by the samples and it did not significantly influence spalling behavior. The smoothness of the platinum surface did however, affect the growth of the alumina scale. The parabolic rate constants for protective oxide growth were lower for the rough specimens indicating more stable oxide development during the steady state growth stage.
- 6 Rumpling was observed on several specimens and does not appear to be a function of pre-aluminizing surface smoothness.
- 7 Smoothing of the platinum surface can have the effect of thinning the plate to a point where it no longer provides the necessary protection, indicating that the thickness of the plate is a variable affecting its protective capabilities.

The following are topics recommended for further study to develop a broader understanding of the effect of platinum surface effects on oxide adherence in a high temperature environment:

- 1 The effect of platinum plate thickness on the cyclic oxidation behavior of both smoothed and rough specimens.
- 2 The effect of post-aluminizing surface roughness on oxide adherence characteristics.
- 3 The actual structure of the oxide-scale interface should be examined by a deep etching technique to evaluate the role of roughness in promoting oxide adherence.
- 4 The oxide formed on the platinum modified aluminum diffusion coatings should be examined by x-ray diffraction and microprobe analysis to aid in the understanding of the oxide growth mechanisms and the changes that occur during cyclic oxidation.

# APPENDIX A

## TABLES I-V

TABLE I  
IN-738 NOMINAL COMPOSITION (WEIGHT PERCENT)

Ni	bal.	Cr	16.0	Co	8.5
Mo	1.75	W	2.6	Ti	3.4
Al	3.4	Nb	0.9	Ta	1.75
C	0.17	B	0.01	Zr	0.10
Fe	0.5 max	Mn	0.2 max	Si	0.3 max

TABLE II  
PRE-ALUMINIZING HEAT TREATMENTS

CODE	HEAT TREATMENT
1	1/2 hour at 870°C
2	2 hours at 980°C
3	3 hours at 1040°C
4	4 hours at 1080°C



TABLE III  
CODING SYSTEM FOR CONVENTIONAL AND PLATINUM MODIFIED  
ALUMINIDE COATINGS

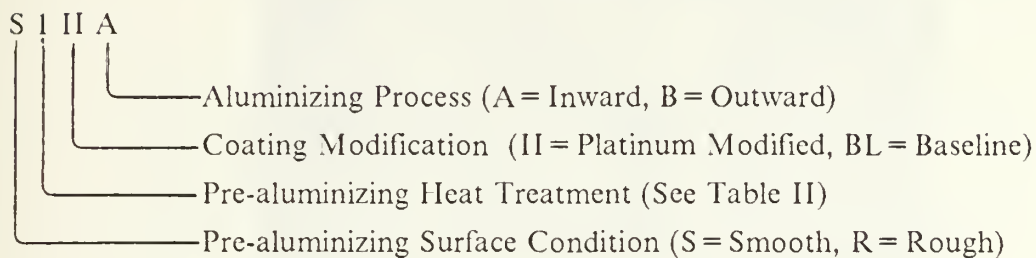


TABLE IV  
SPECIMEN LISTING

Specimen Number	Code	Specimen Number	Code
3	R1IIB	11	R3IIB
4	S1IIB	12	S3IIB
7	R2IIB	15	R4IIB
8	S2IIB	16	S4IIB
9	R3IIA	17	BLA
10	S3IIA	18	BLB

TABLE V  
PARABOLIC RATE CONSTANTS

( $K_p$  in  $\text{g}^2\text{cm}^4\text{s}^{-1}$ )

R1IIB	$6.3 \times 10^{-13}$
S1IIB	$1.05 \times 10^{-12}$
R2IIB	$6.3 \times 10^{-13}$
S2IIB	$1.24 \times 10^{-12}$
R3IIA	$9.4 \times 10^{-13}$
S3IIA	$9.1 \times 10^{-13}$
R3IIB	$6.5 \times 10^{-13}$
S3IIB	$1.12 \times 10^{-12}$
R4IIB	$1.78 \times 10^{-12}$
S4IIB	$6.6 \times 10^{-13}$

APPENDIX B  
FIGURES

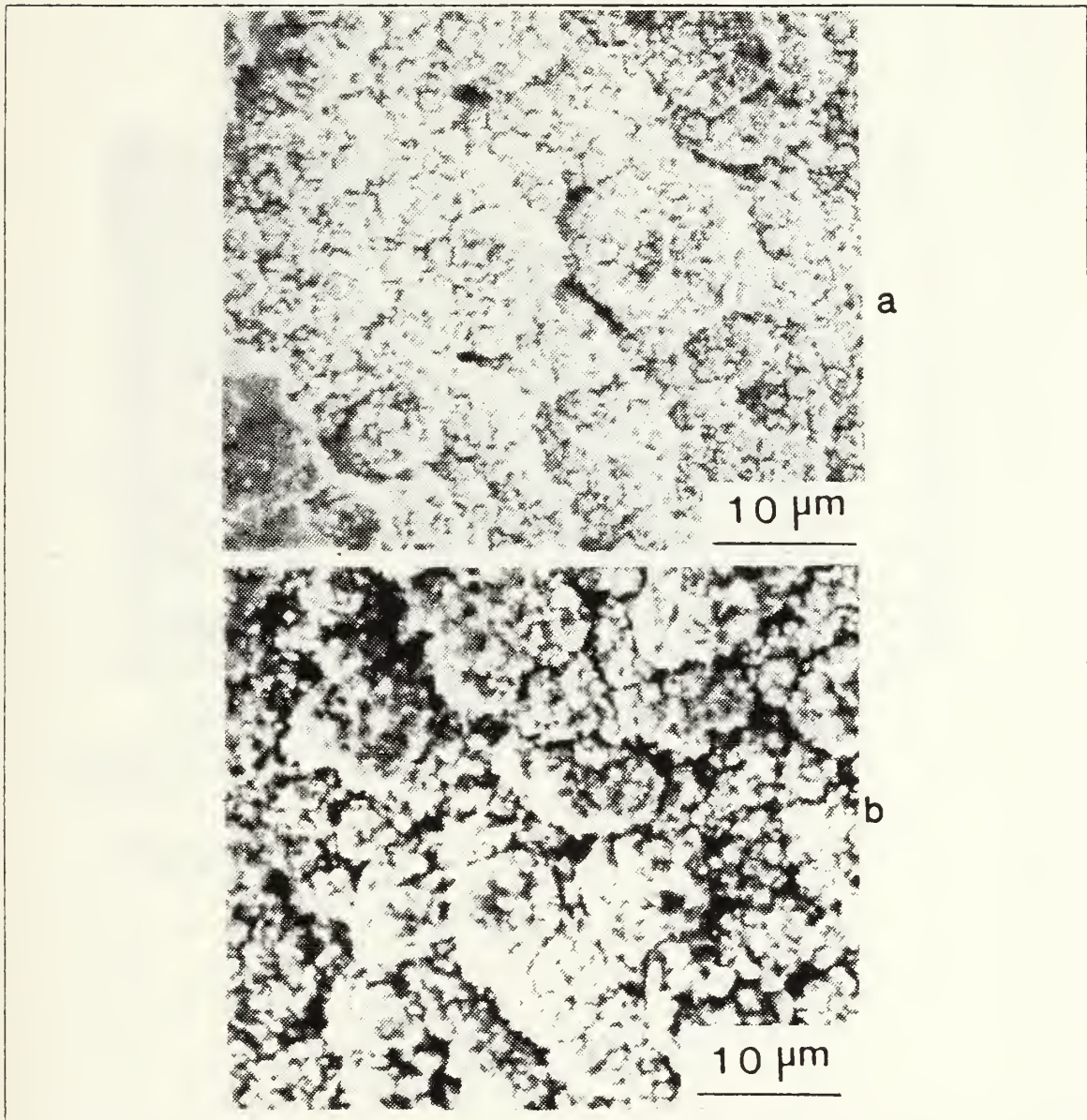


Figure B.1 Scanning Electron Microscope Photomicrograph of (a) Platinum plate on nickel base superalloy and (b) same specimen after 2 hours at 980°C diffusion heat treatment.

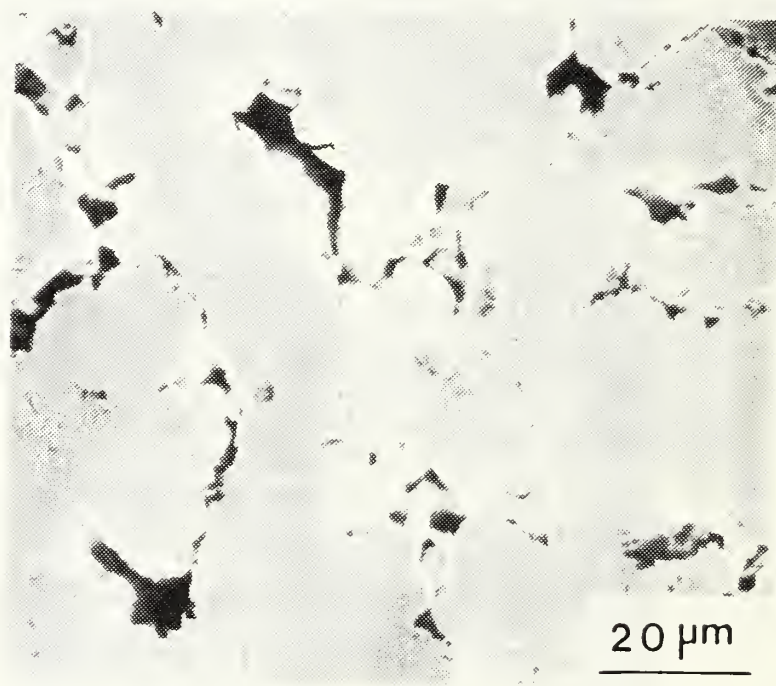


Figure B.2 Scanning Electron Photomicrograph of platinum plated specimen (S311A) after smoothing process.



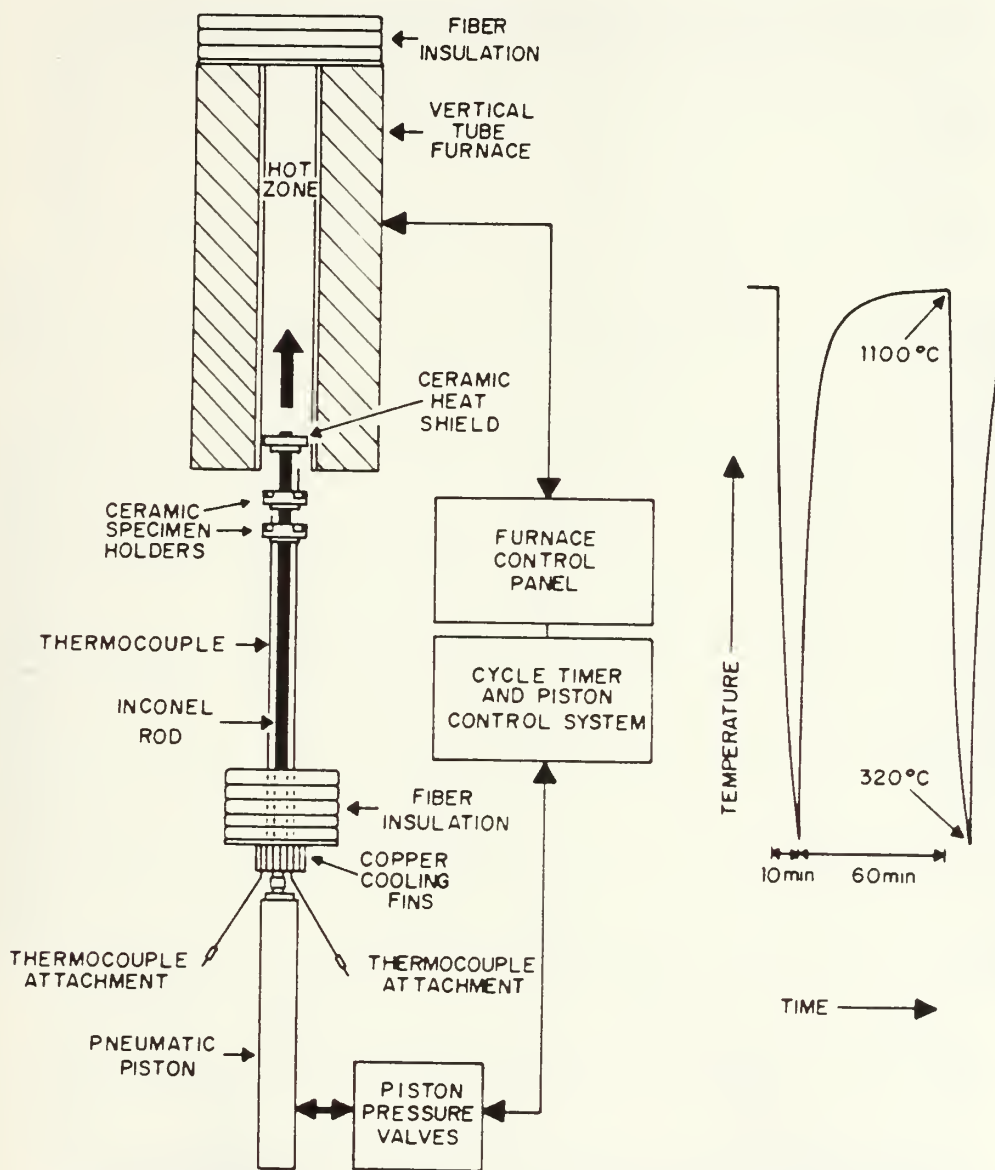


Figure B.3 Vertical Oven Configuration and Heating--Cooling Cycle.

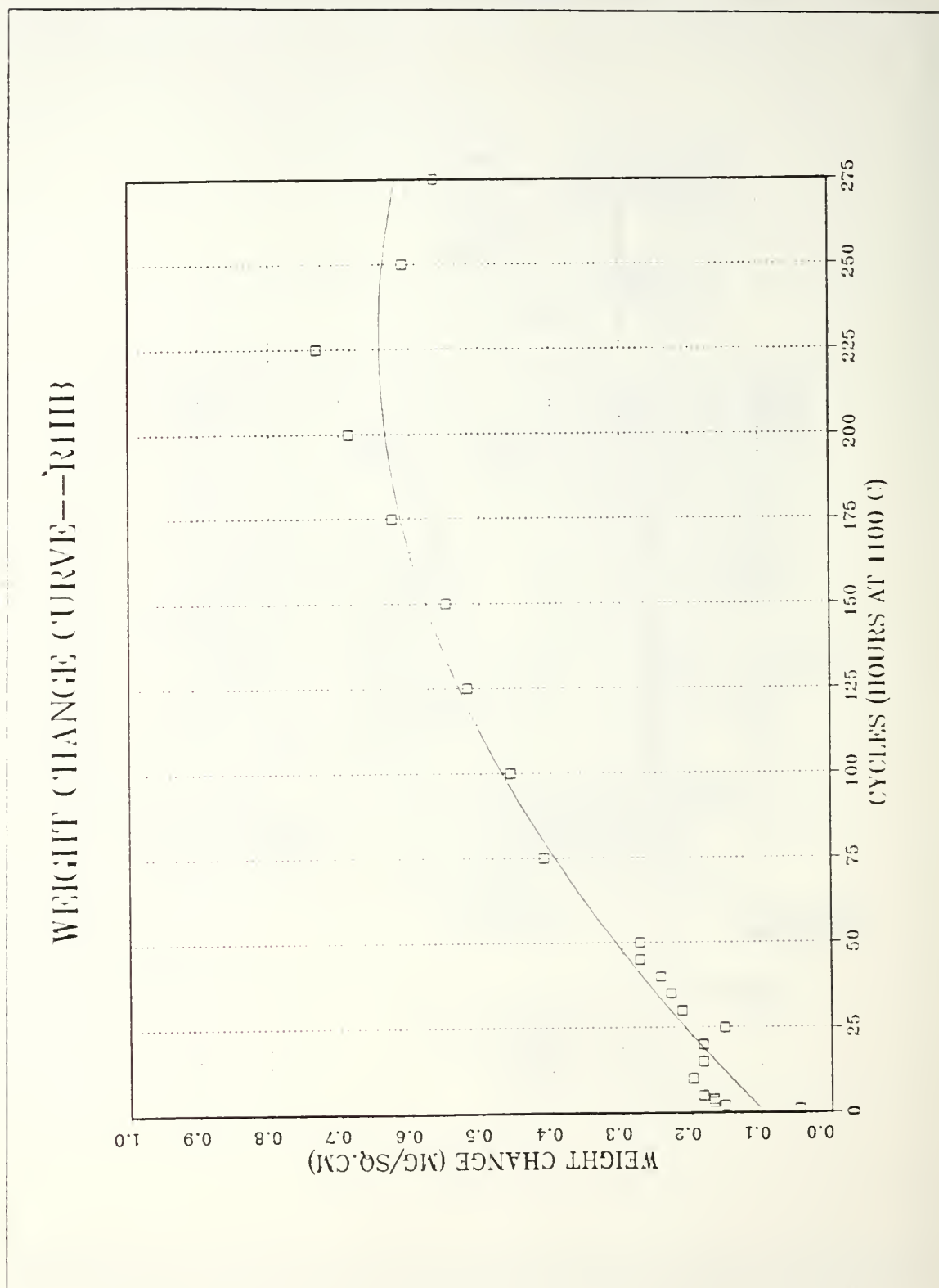


Figure B.4 Weight Change Curve for Specimen R111B.

# WEIGHT CHANGE CURVE--S111B

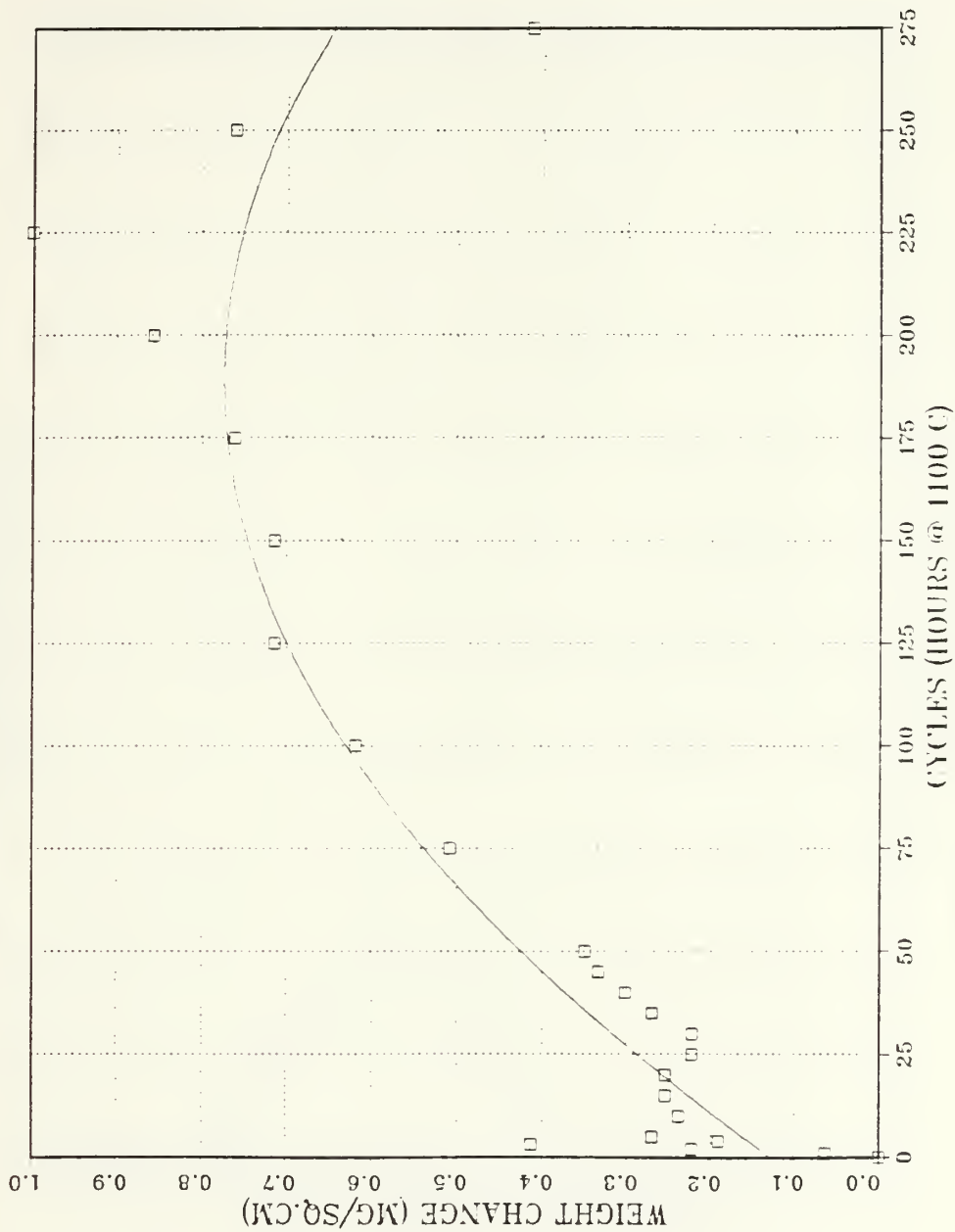


Figure B.5 Weight Change Curve for Specimen S111B.

# WEIGHT CHANGE CURVE--R211B

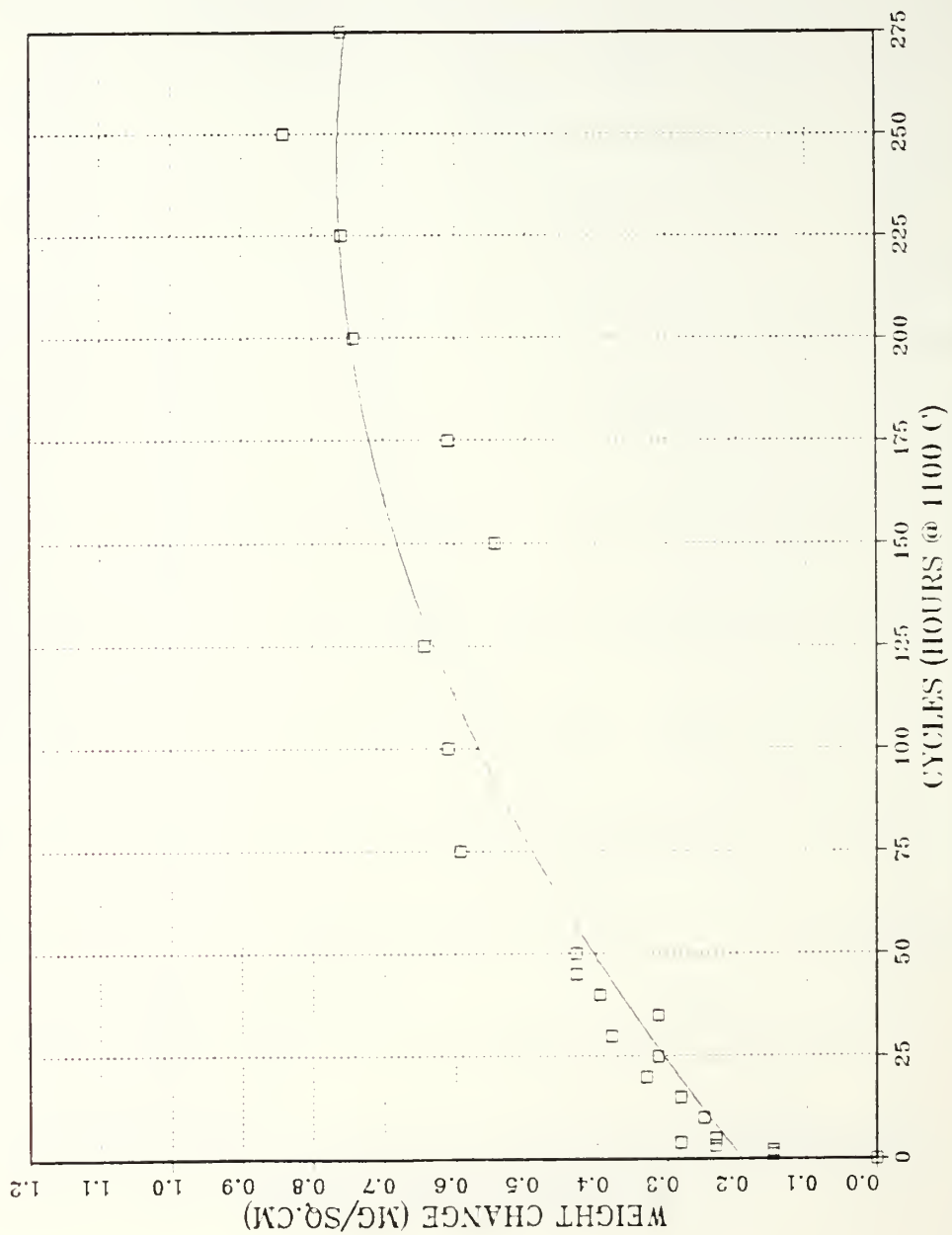


Figure B.6 Weight Change Curve for Specimen R211B.



# WEIGHT CHANGE CURVE--S2IIB

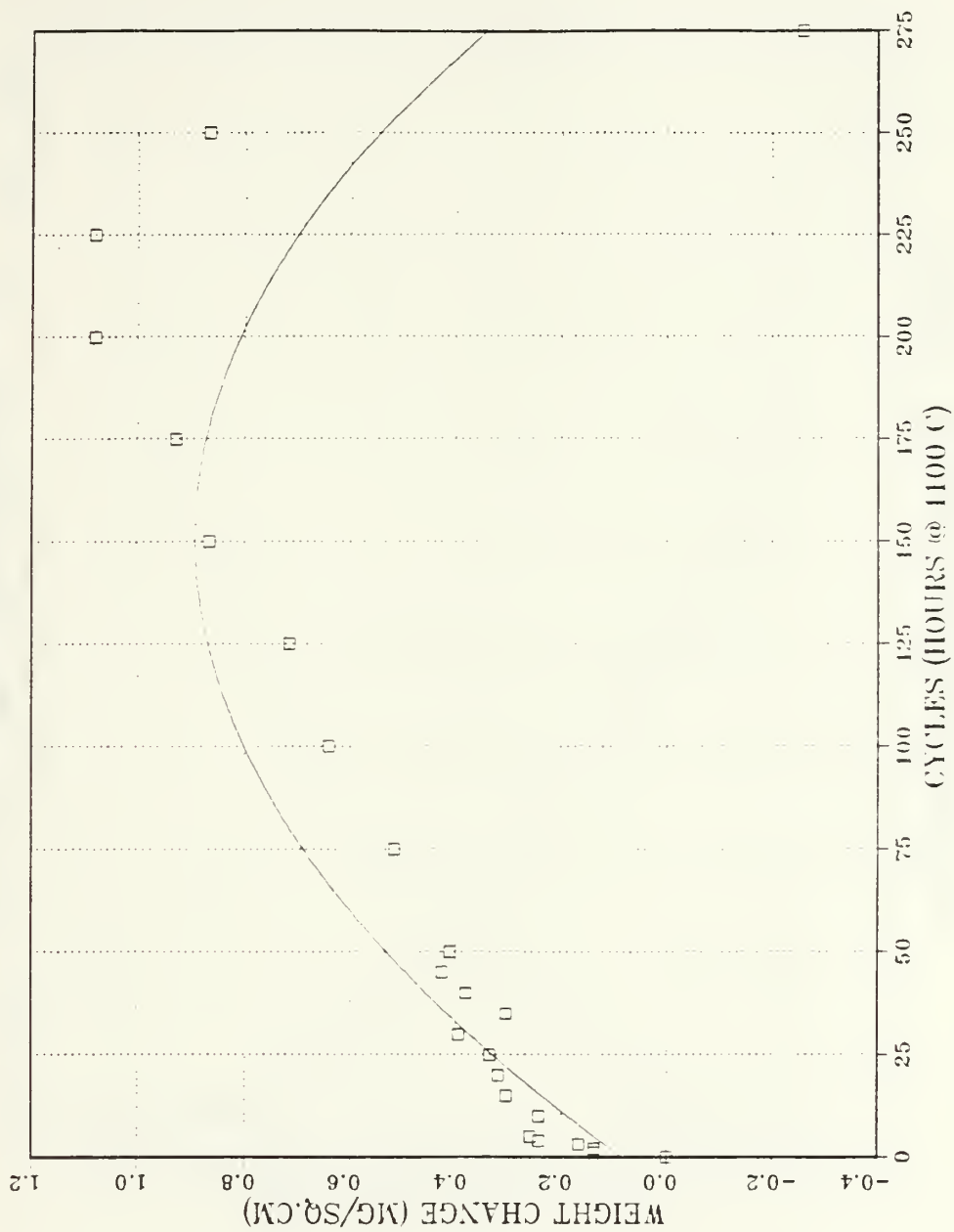


Figure B.7 Weight Change Curve for Specimen S2IIB.

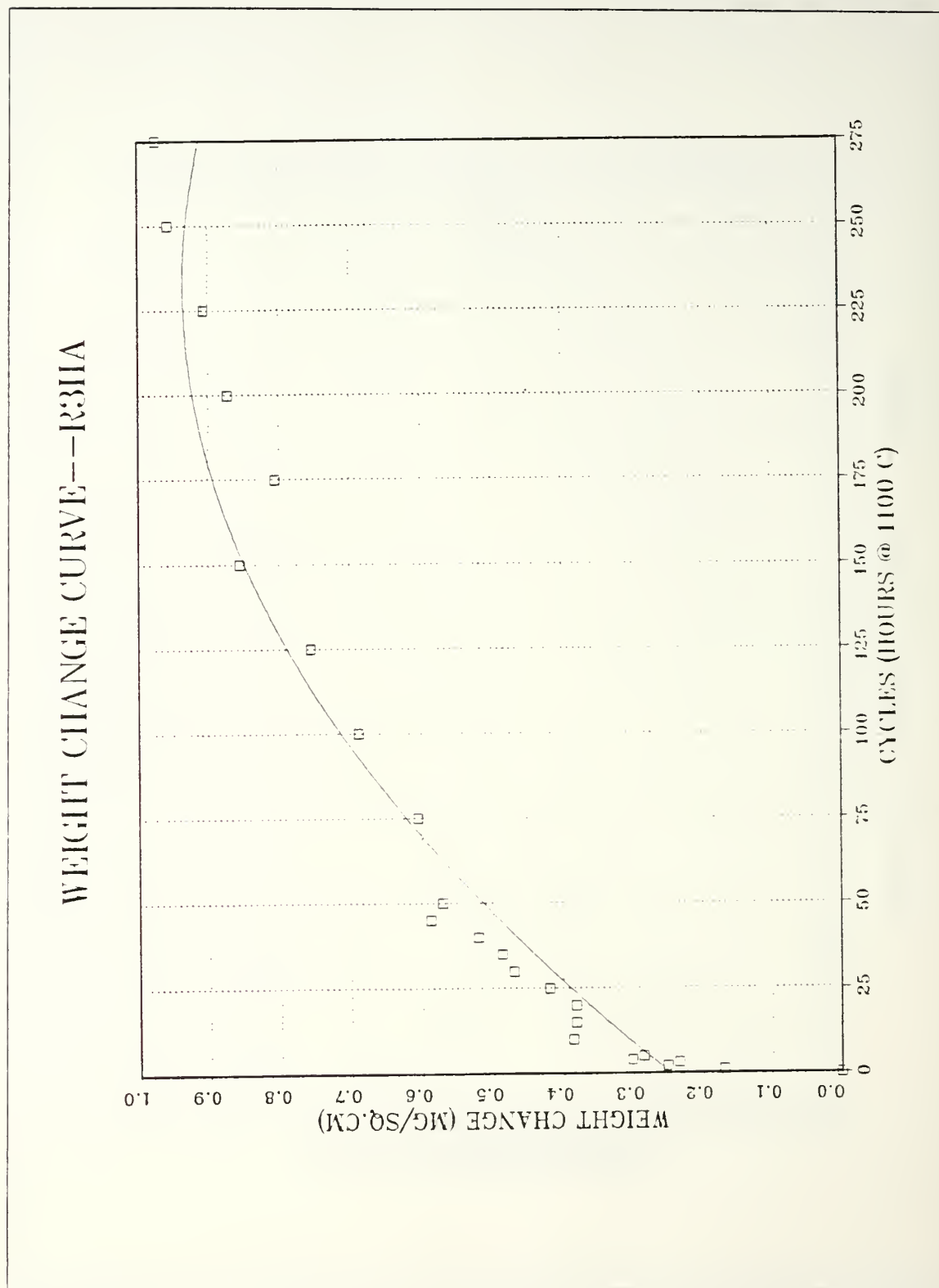


Figure B.8 Weight Change Curve for Specimen R311A.

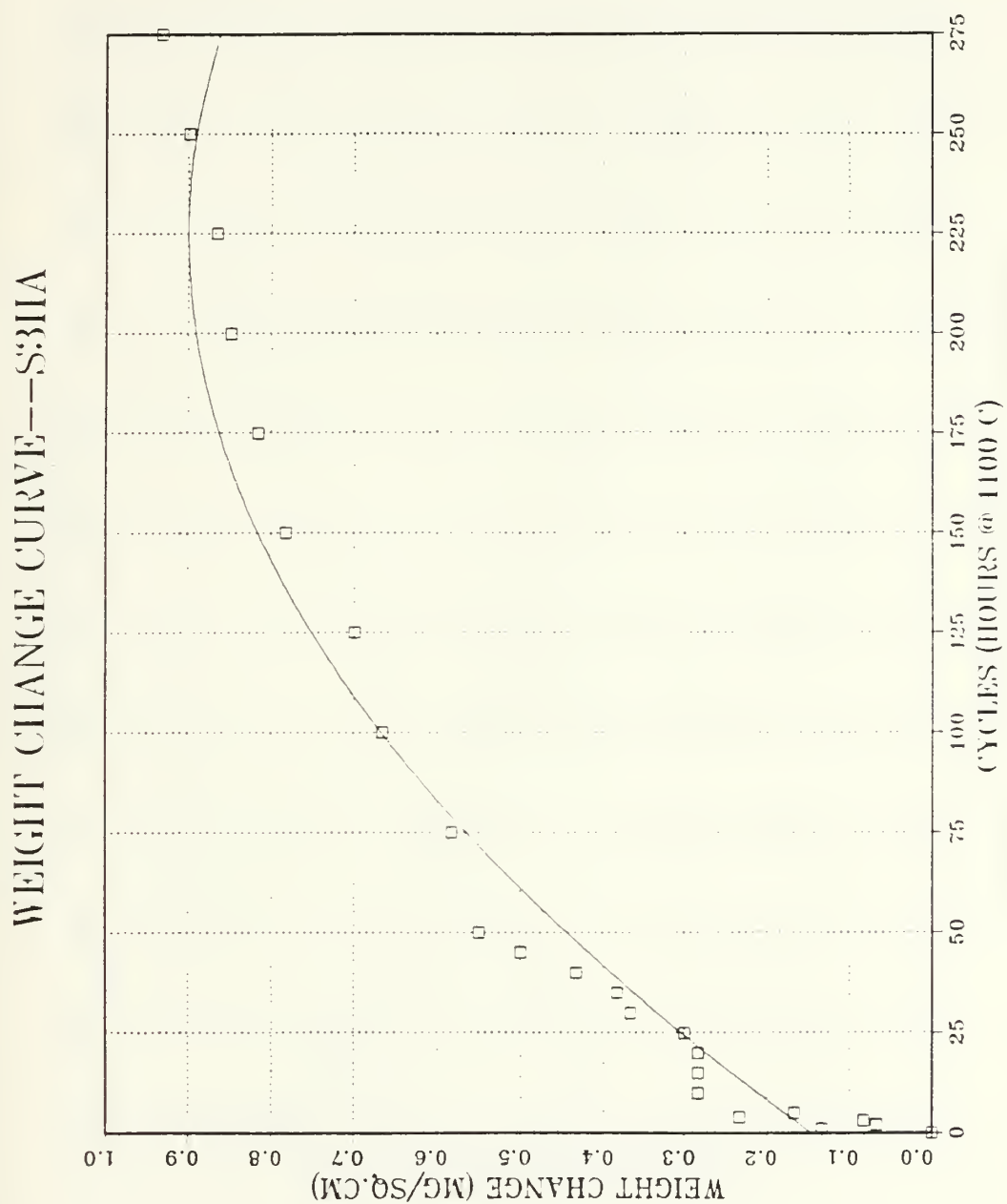


Figure B.9 Weight Change Curve for Specimen S3IIA.

# WEIGHT CHANGE CURVE--R3IIB

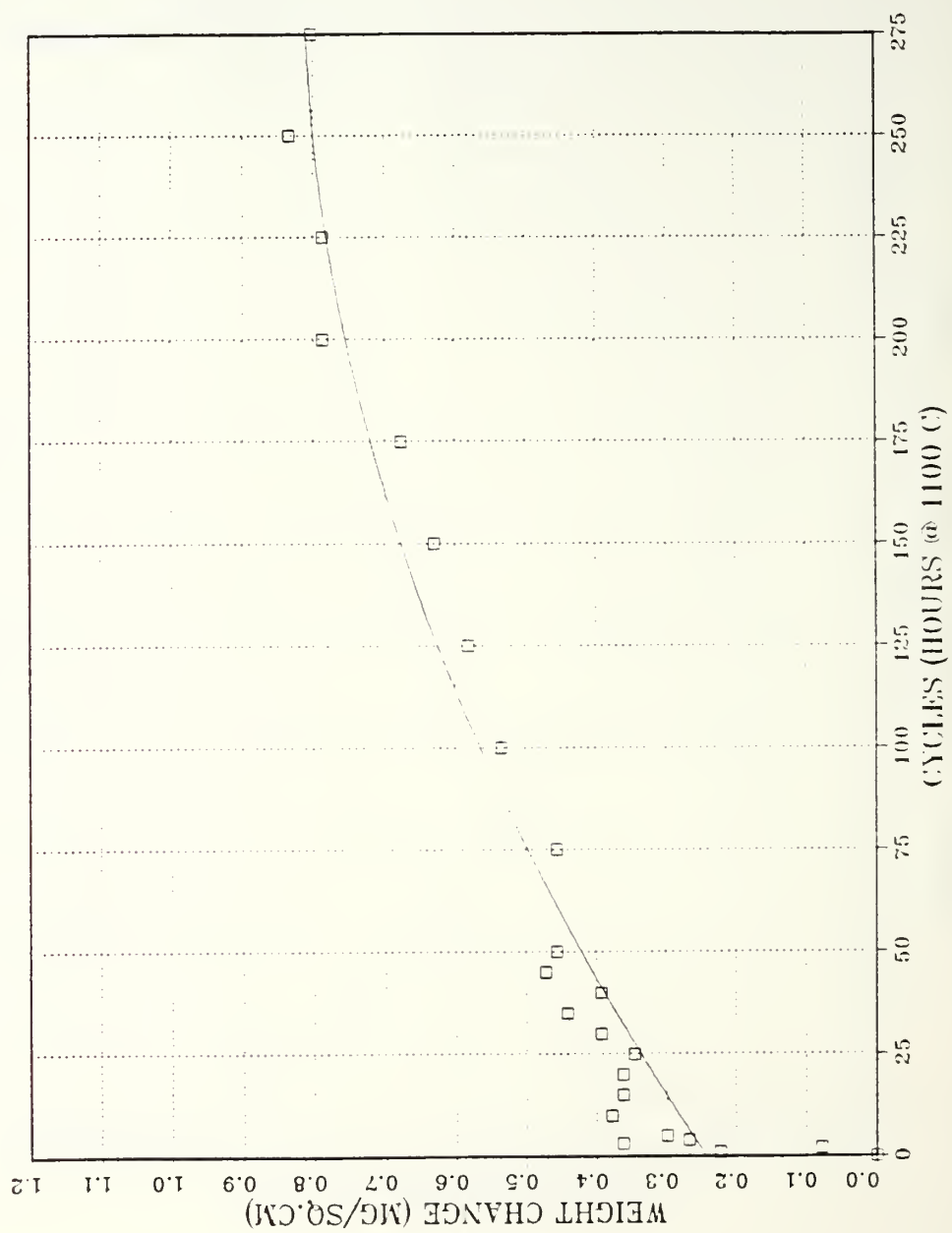


Figure B.10 Weight Change Curve for Specimen R3IIB.



# WEIGHT CHANGE CURVE--S3IIB

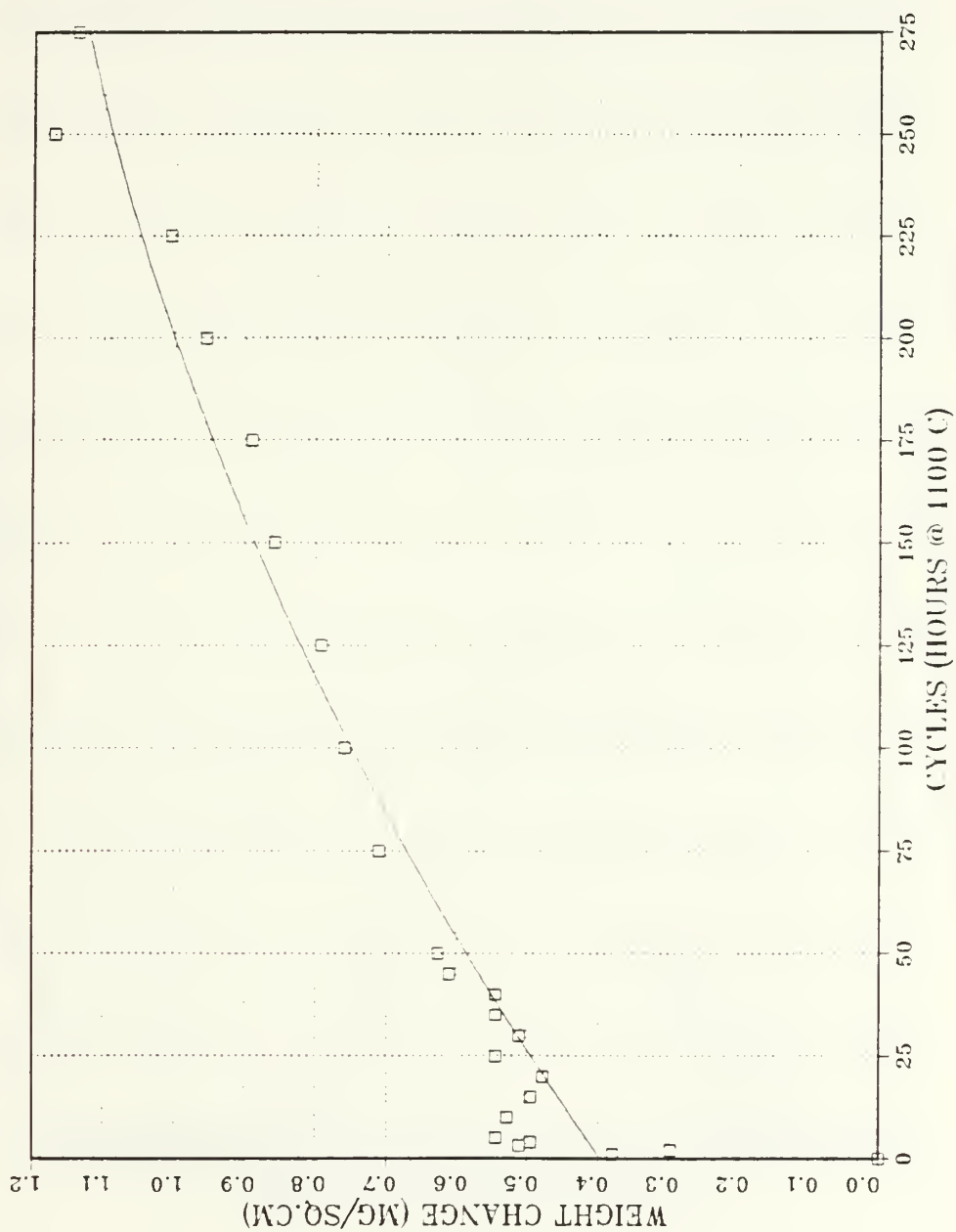


Figure B.II Weight Change Curve for Specimen S3IIB.

# WEIGHT CHANGE CURVE--R4IIB

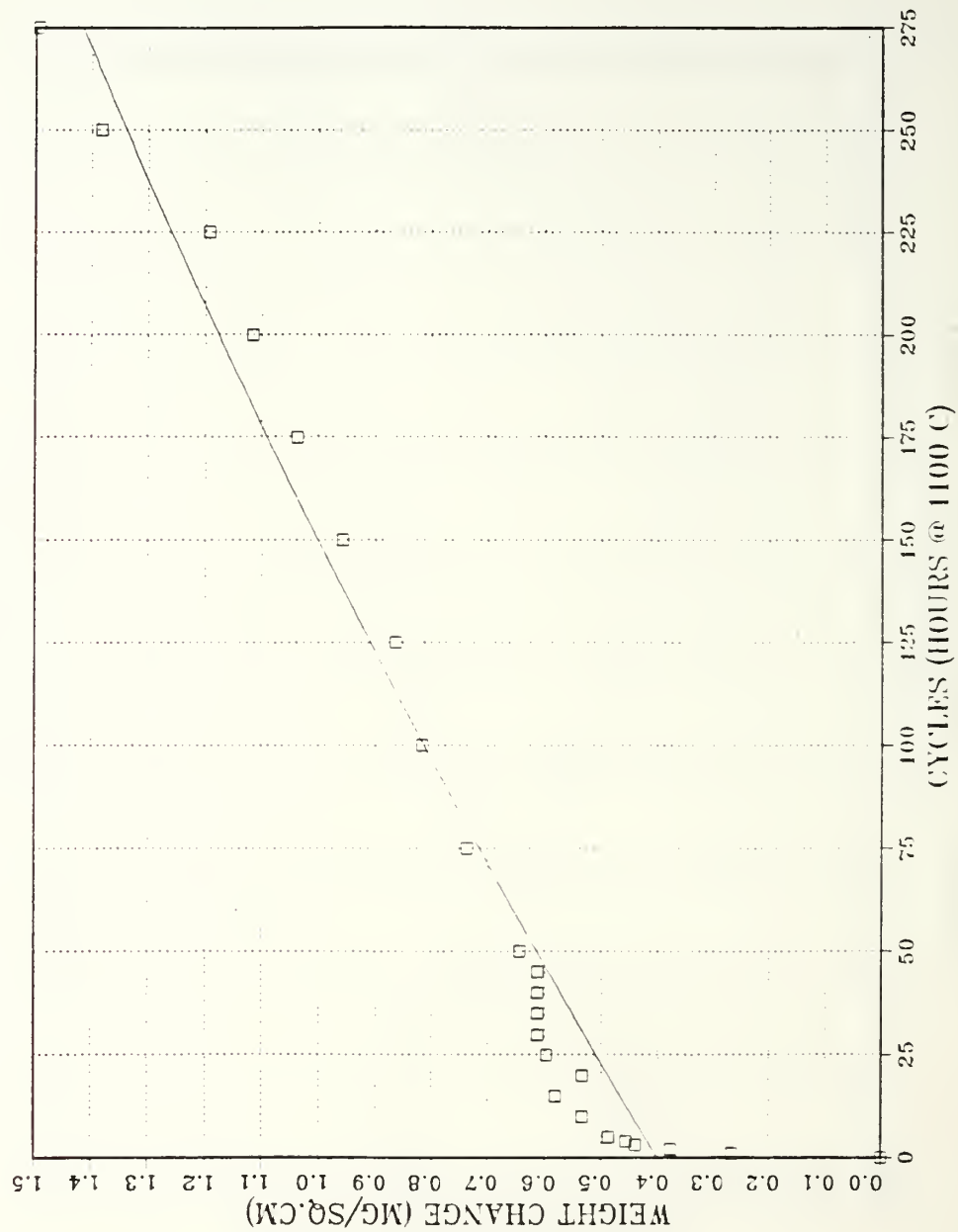


Figure B.12 Weight Change Curve for Specimen R4IIB.

# WEIGHT CHANGE CURVE--S4IIB

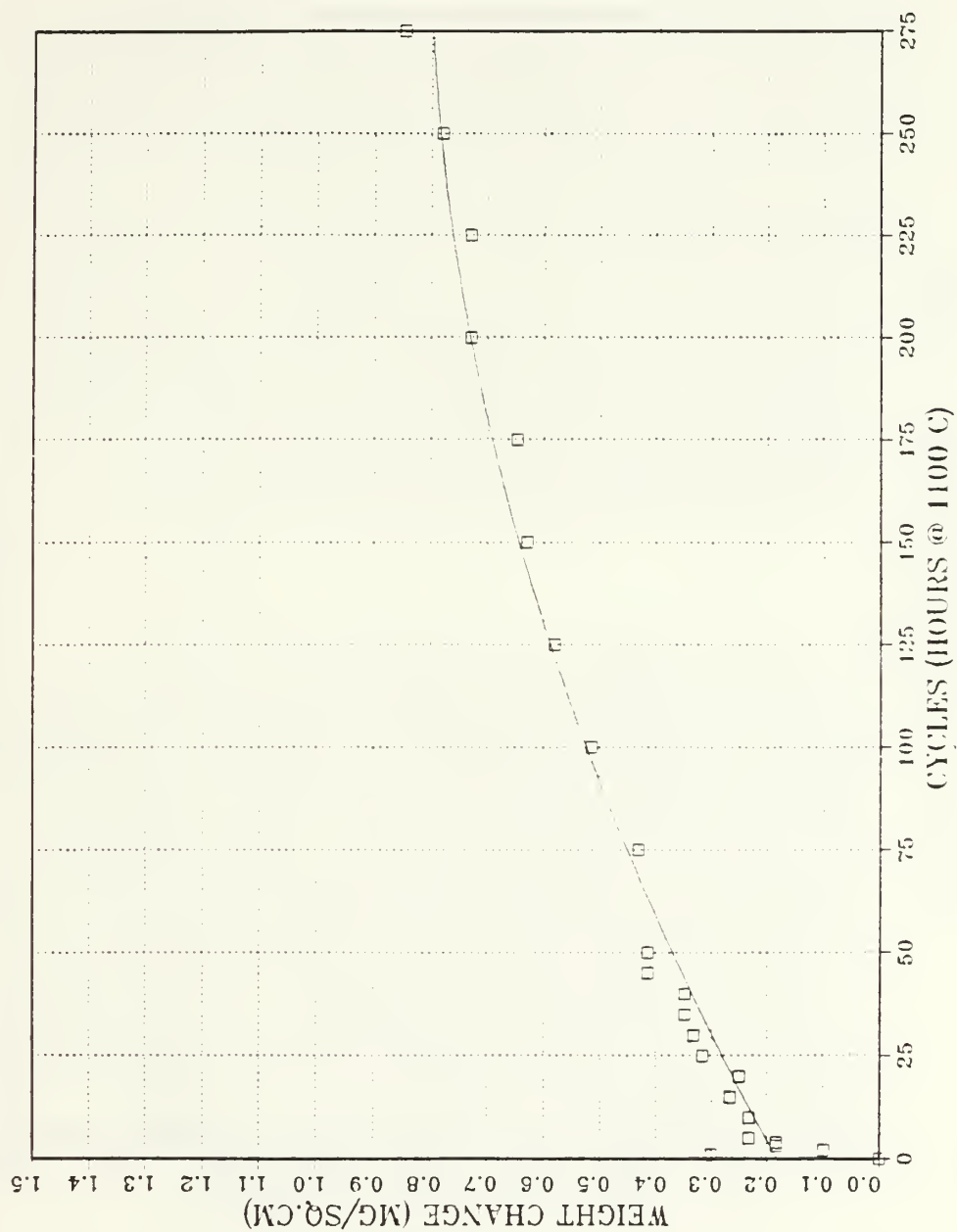


Figure B.13 Weight Change Curve for Specimen S4IIB.

WEIGHT CHANGE CURVE--BLA

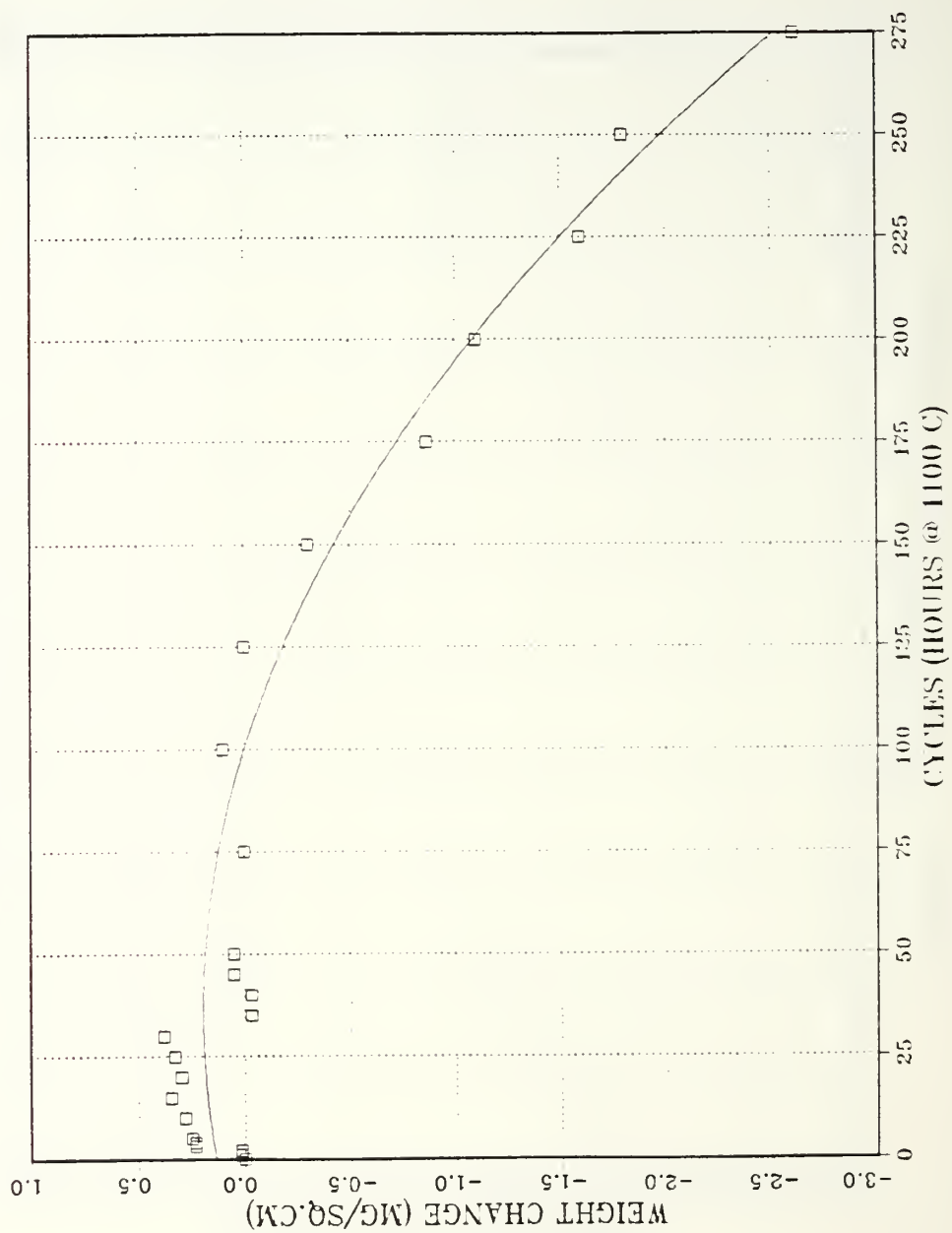


Figure B.14 Weight Change Curve for Specimen BLA.



# WEIGHT CHANGE CURVE--BLB

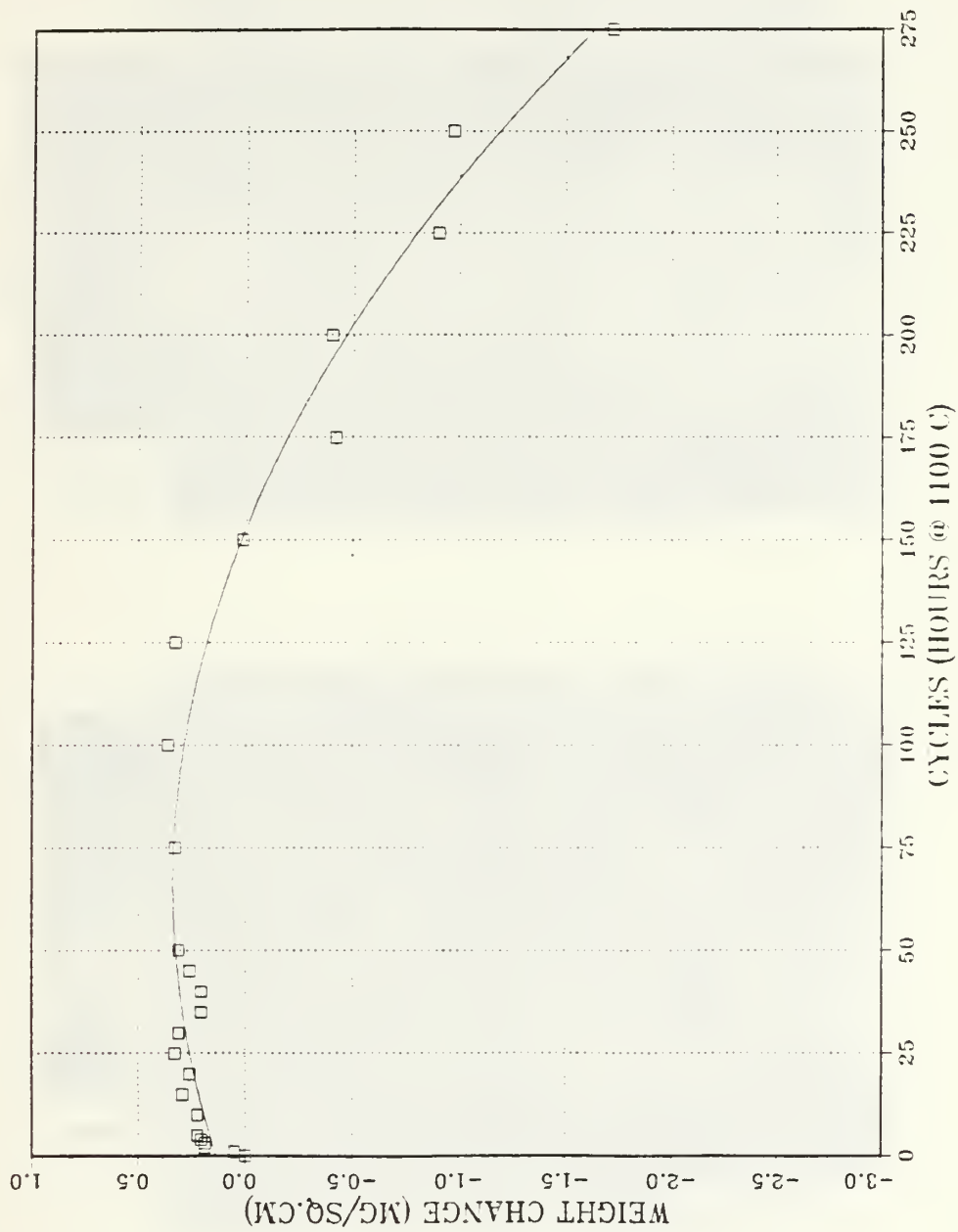


Figure B.15 Weight Change Curve for Specimen BLB.

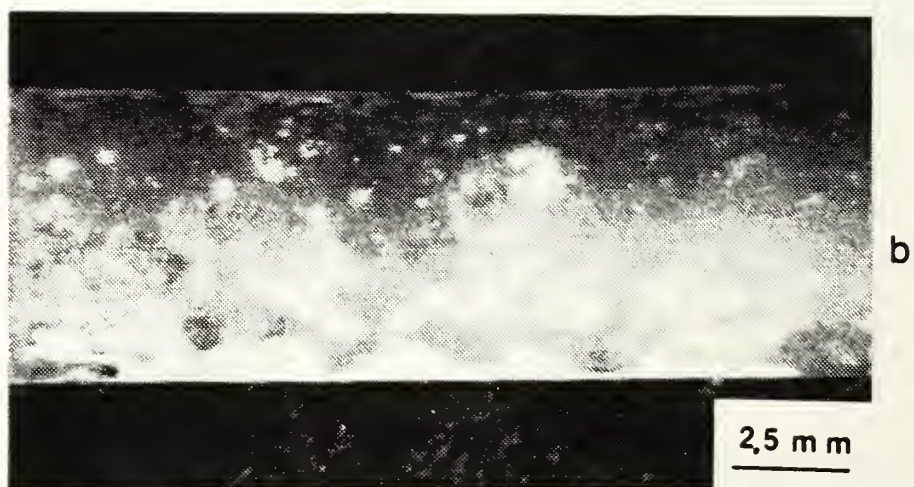
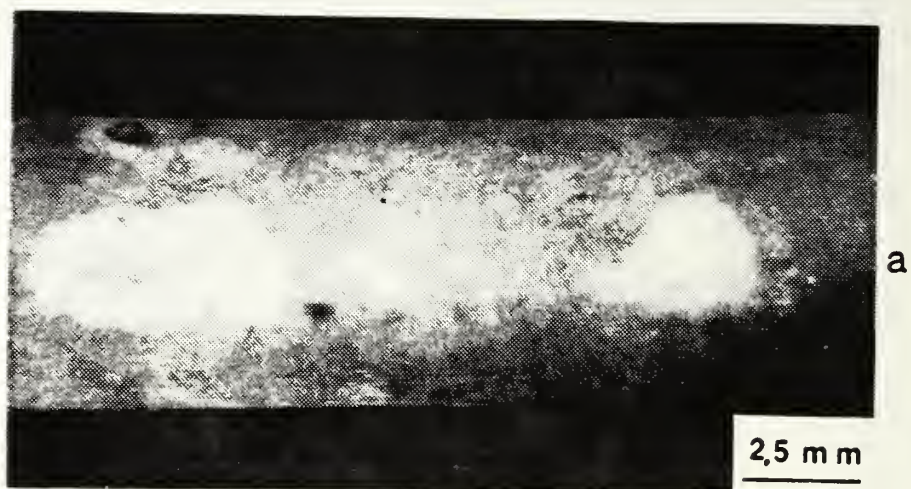


Figure B.16 Surface micrographs of specimens (a) S111B and (b) R311B after 50 hours of cyclic oxidation testing.

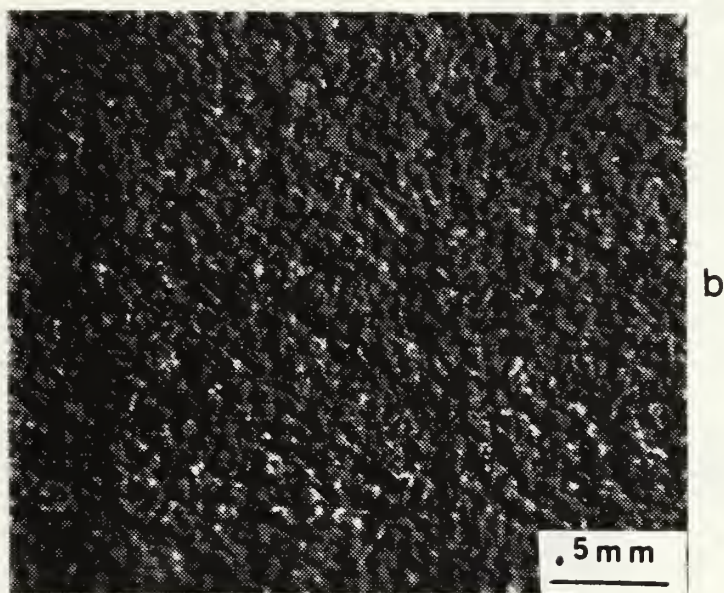
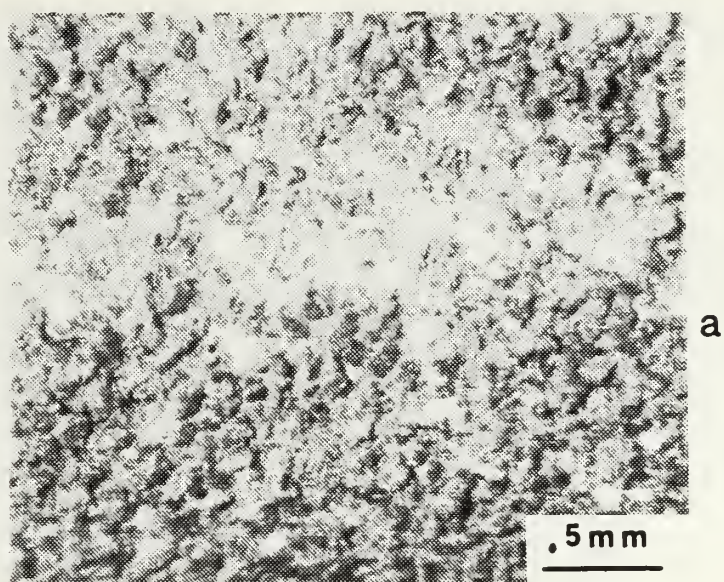


Figure B.17 Surface micrographs showing spalling and deformation on specimens (a) S211B and (b) S311B after 275 cycles at 1100°C.



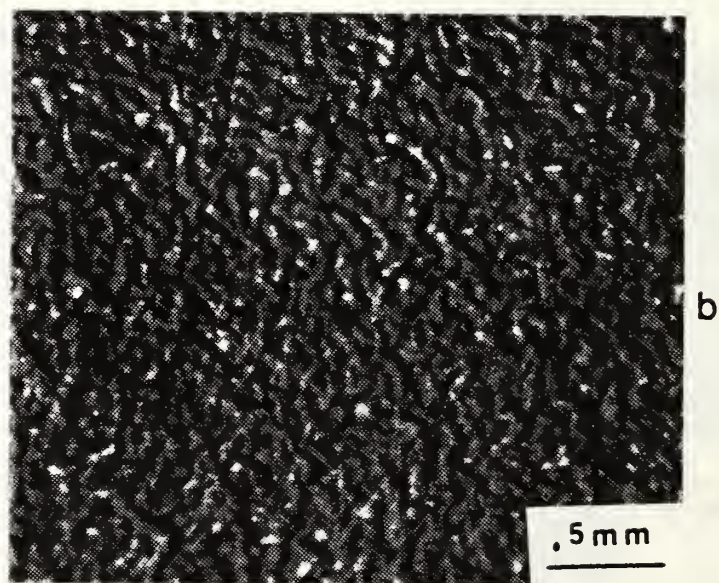
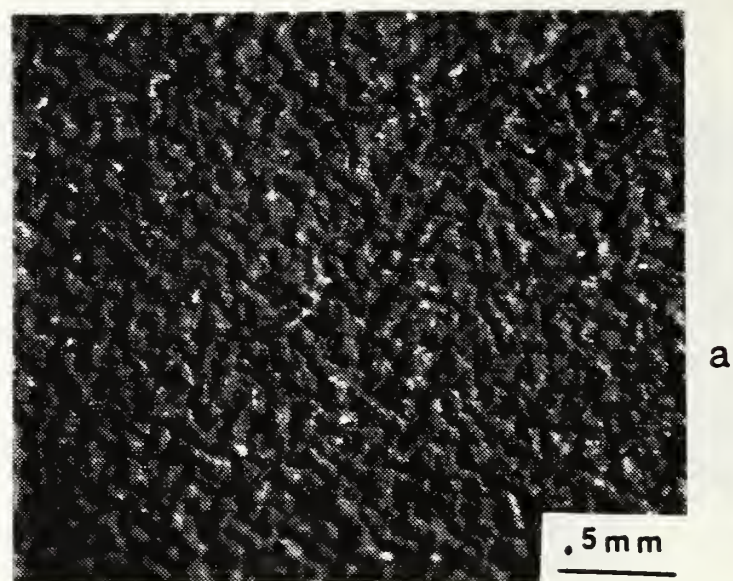


Figure B.18 Surface micrographs showing spalling and deformation on the conventional aluminide coatings, specimens (a) BLA and (b) BLB after 275 cycles at 1100°C.



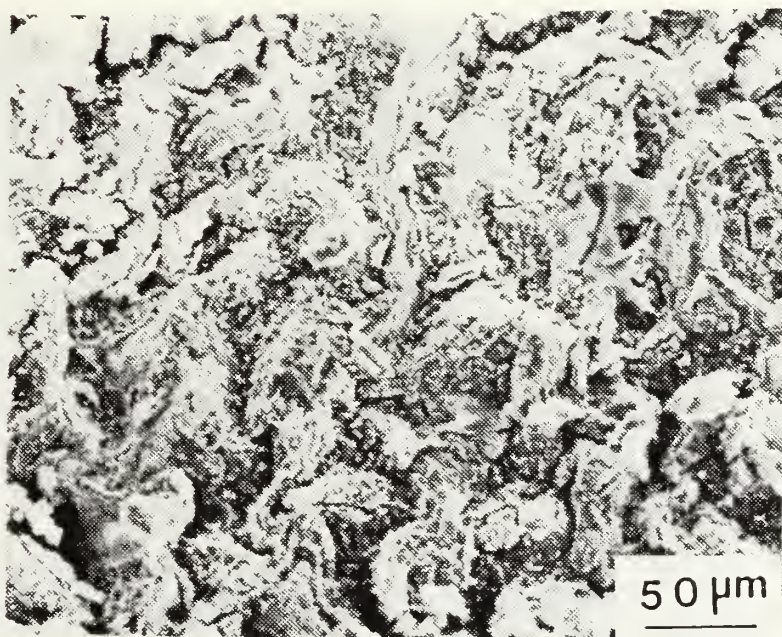
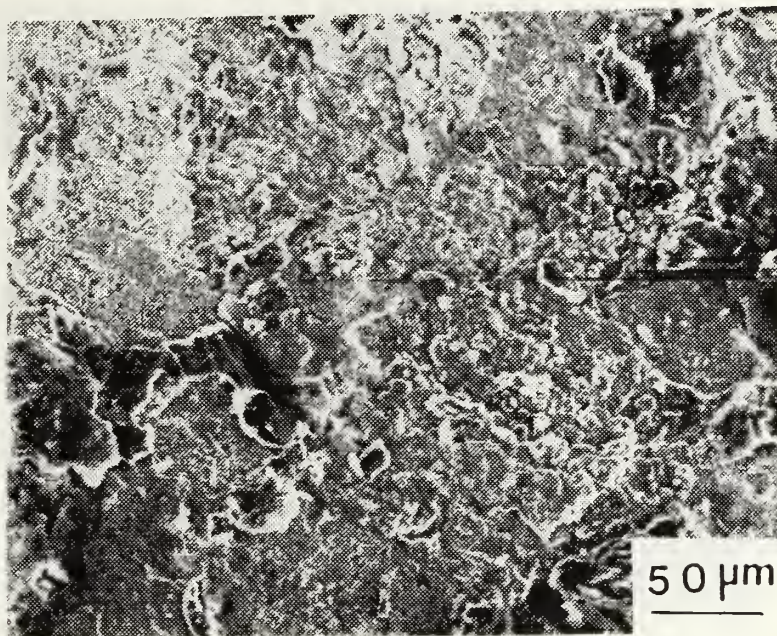


Figure B.19 SEM surface photomicrographs of specimens (a) S211B and (b) R311A after 275 cycles at 1100°C.



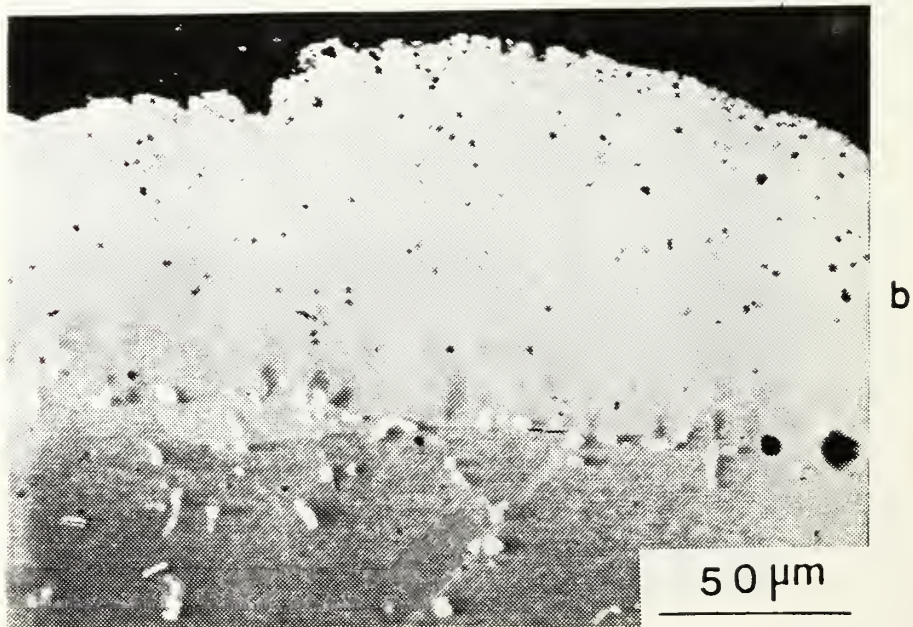
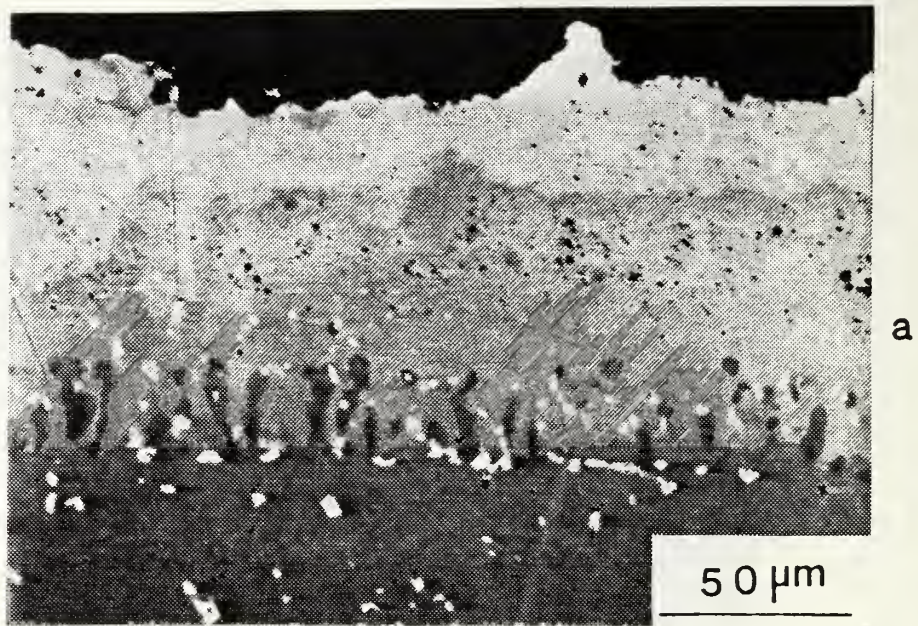


Figure B.20 SEM cross section photomicrographs of specimens (a) R111B and (b) S111B after 275 cycles at 1100°C.



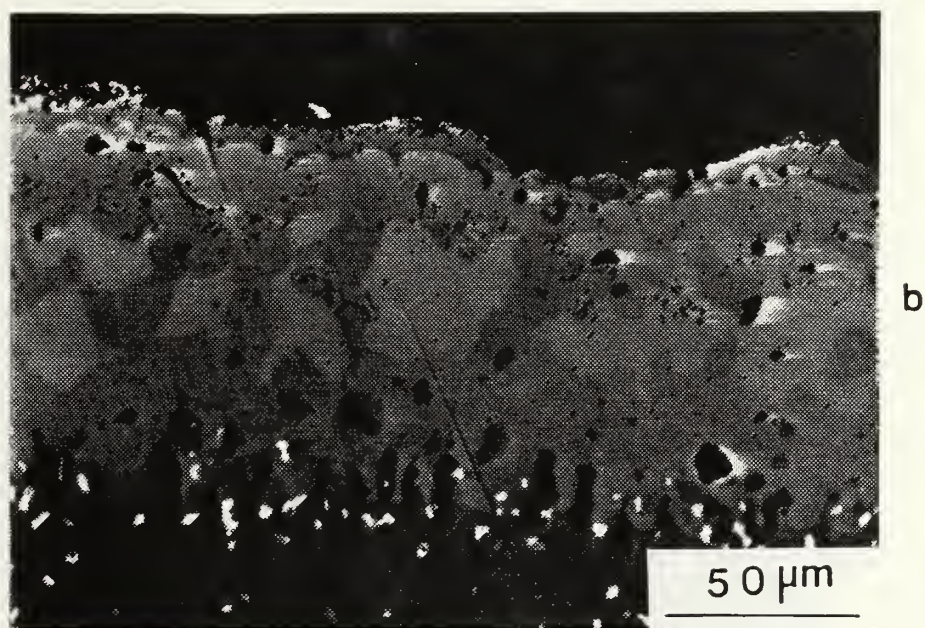
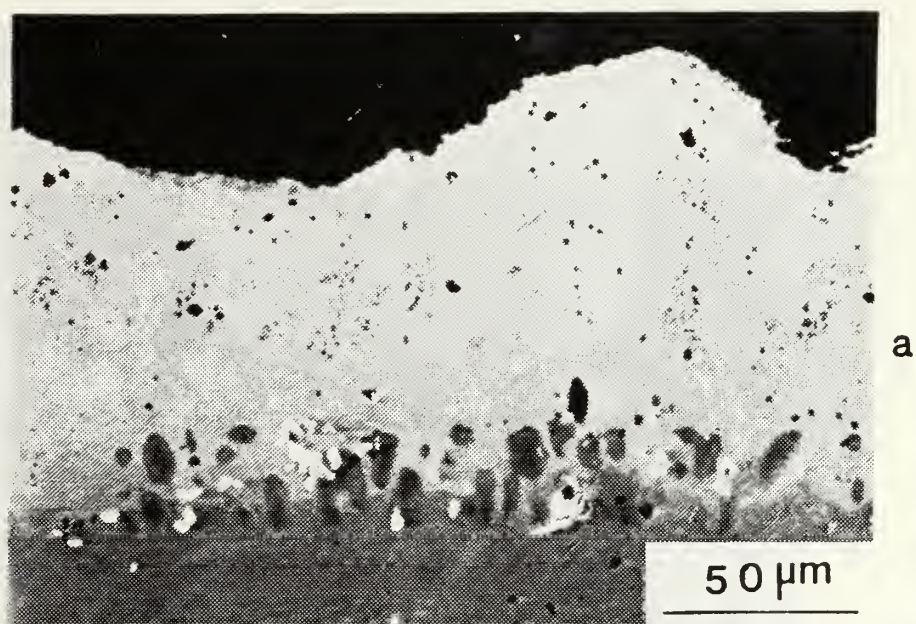


Figure B.21 SEM cross section photomicrographs of specimens (a) R211B and (b) S211B after 275 cycles at 1100°C.



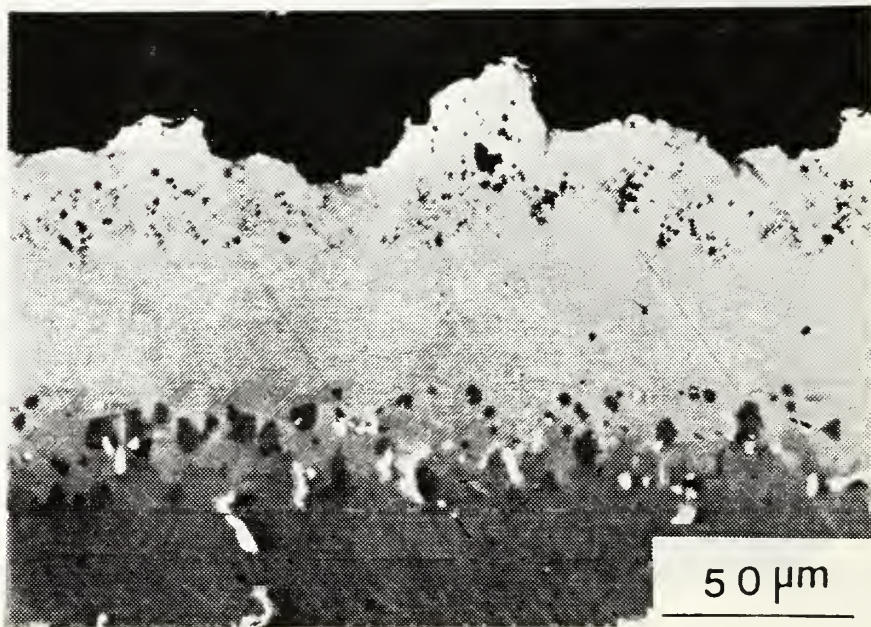
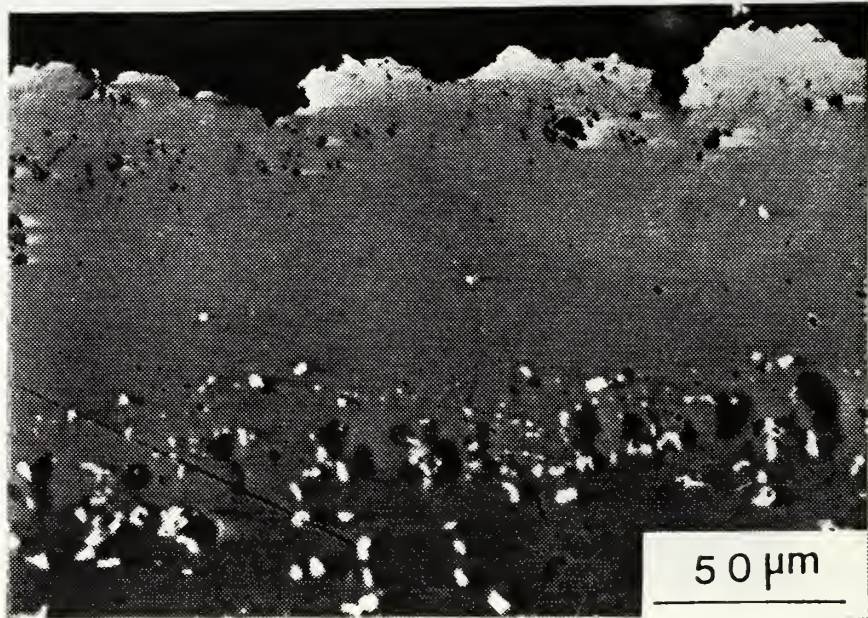


Figure B.22 SEM cross section photomicrographs of specimens (a) R311A and (b) S311A after 275 cycles at 1100 °C.



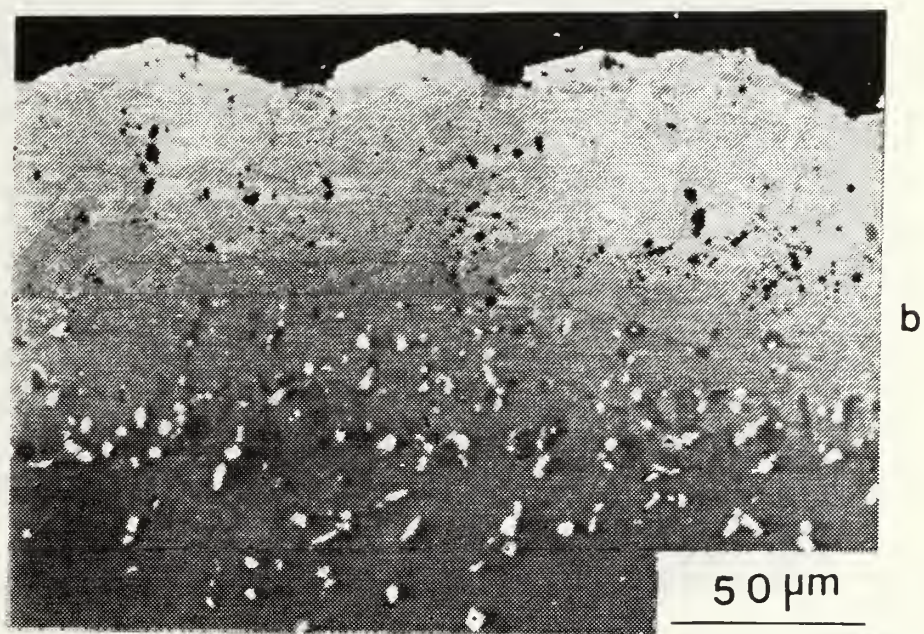
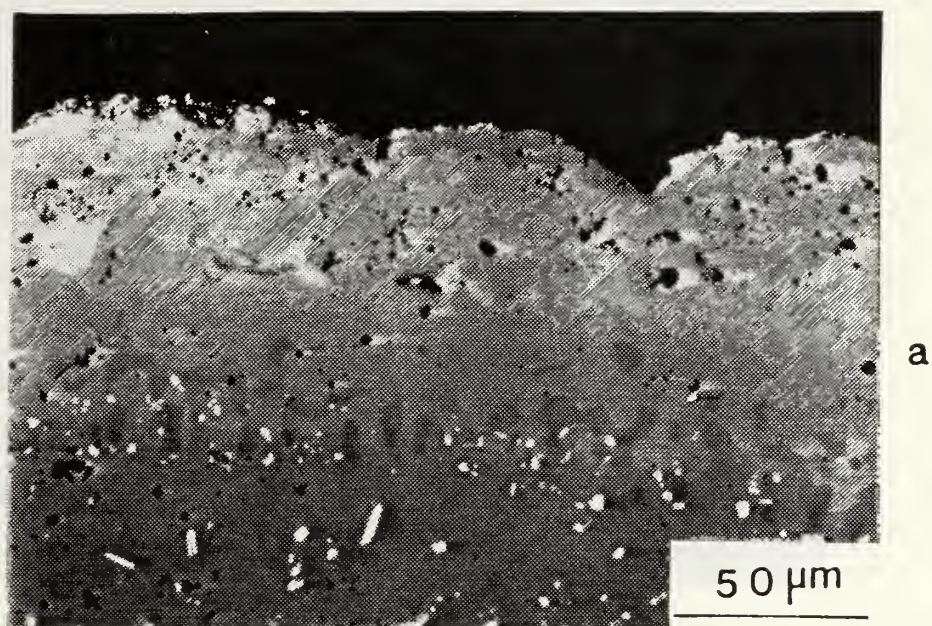


Figure B.23 SEM cross section photomicrographs of specimens (a) R311B and (b) S311B after 275 cycles at 1100°C.



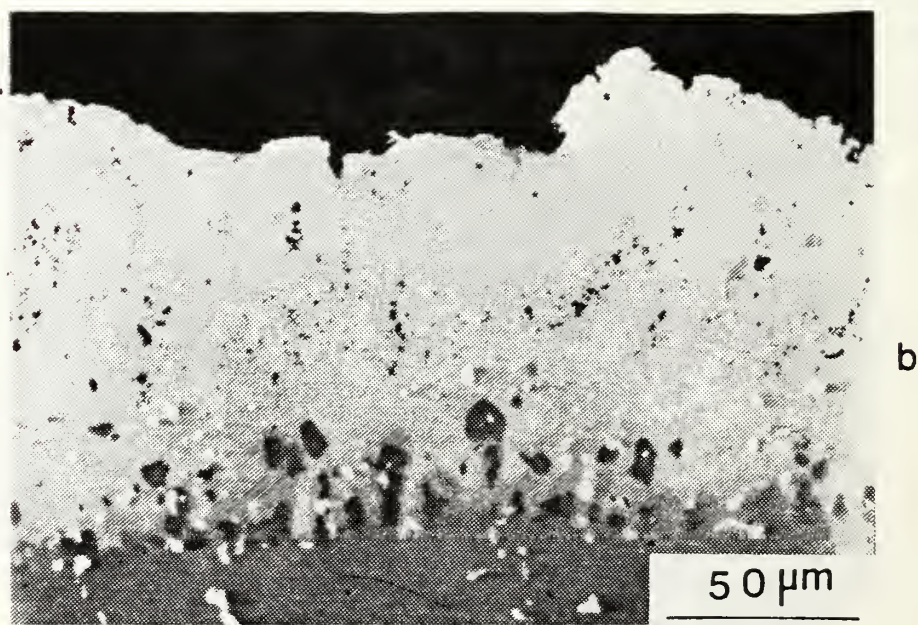
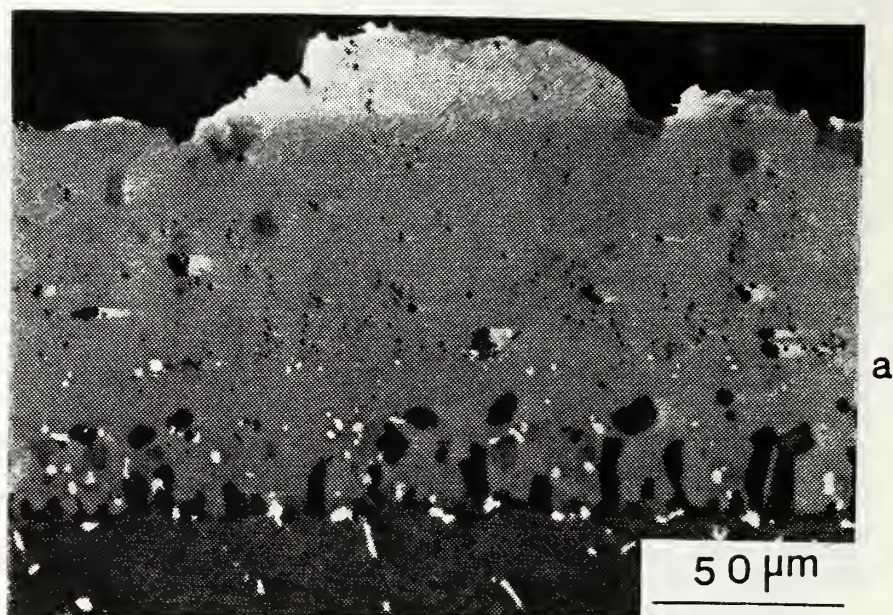


Figure B.24 SEM cross section photomicrographs of specimens (a) R411B and (b) S411B after 275 cycles at 1100°C.



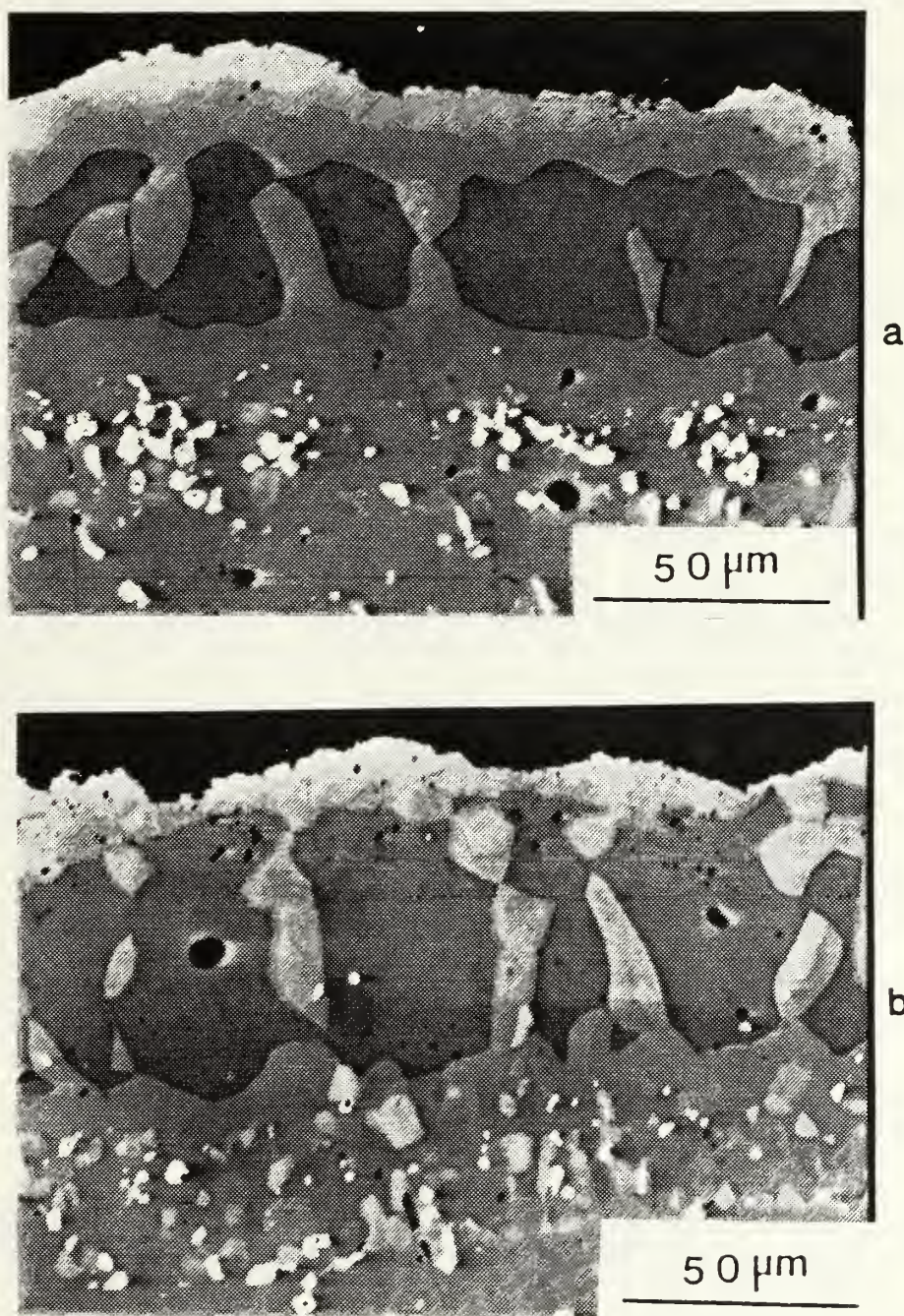


Figure B.25 SEM cross section photomicrographs of the baseline specimens, (a) BLA and (b) BLB after 275 hours at 1100°C.

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